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REDOX TECHNICAL MANUAL

Chemical Development Section
Separations Technology Division
Technical Divisions

July 10, 1951

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CONTENTS

		Page
PART I:	INTRODUCTION	101
Chapter I.	Introduction	101
PART II:	PROCESS	201
Chapter II.	Irradiated Slugs and Fission-Product Decay	201
Chapter III.	Feed Preparation	301
Chapter IV.	Process Chemistry (Solvent-Extraction)	401
Chapter V.	Process Engineering (Solvent-Extraction)	501
Chapter VI.	Solvent-Extraction Procedure	601
Chapter VII.	Plutonium Concentration	701
Chapter VIII.	Aqueous Make-Up	801
Chapter IX.	Solvent Treatment	901
Chapter X.	Waste Treatment and Disposal	1001
PART III:	PLANT AND EQUIPMENT	1101
Chapter XI.	General Description of the Plant	1101
Chapter XII.	Engineering Flow Diagrams	1201
Chapter XIII.	Tanks	1301
Chapter XIV.	Solvent-Extraction Columns	1401
Chapter XV.	Gas Scrubbing, Concentration, and Distillation Equipment	1501
Chapter XVI.	Other Process Equipment	1601
Chapter XVII.	Pumps and Jets	1701
Chapter XVIII.	Remote Operation and Maintenance	1801
PART IV:	PROCESS CONTROL	1901
Chapter XIX.	Instrumentation	1901
Chapter XX.	Analytical Methods	2001
PART V:	SAFETY	2101
Chapter XXI.	Health Protection from Radiations	2101
Chapter XXII.	Shielding	2201
Chapter XXIII.	Decontamination of Surfaces	2301
Chapter XXIV.	Hazards Other Than Radiation	2401
Chapter XXV.	Critical Mass Control	2501
APPENDIX A:	NUCLEONICS	2601
INDEX		2701

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PART I: INTRODUCTION

CHAPTER I. INTRODUCTION

CONTENTS

Page

A. PURPOSE, SCOPE, AND ARRANGEMENT OF THE MANUAL 102

B. FUNCTION OF THE PLANT 103

1. Design Basis 103
2. Feed Material 103
3. Plutonium Product 104
4. Uranium Product 104

C. PRINCIPLES AND OUTLINE OF THE REDOX PROCESS 106

1. Basic Principles 106
2. Feed Preparation 108
3. Solvent-Extraction 109
   - 3.1 First Extraction Cycle 110
   - 3.2 Second and Third Uranium Cycles 110
   - 3.3 Second and Third Plutonium Cycles 111
   - 3.4 Alternative flowsheets 111
4. Solvent Treatment 112
5. Waste Treatment and Disposal 113
6. Off-Standard Streams 113

D. THE REDOX PLANT 114

1. General Plant Layout 114
2. Special Features of the Plant 116
   - 2.1 Continuous processing 116
   - 2.2 Shielding 116
   - 2.3 Remote operation 116
   - 2.4 Remote maintenance 117
   - 2.5 Silo structure 117
   - 2.6 Materials of construction -- equipment 118
   - 2.7 Protective coverings 118
3. Safety Features of the Plant 119
   - 3.1 Critical mass control 119
   - 3.2 Process area ventilation 119
   - 3.3 Fire and explosion protection 119
4. Chemical and Utility Requirements 120
5. In-Process Inventory 120

REFERENCES 121

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10

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CHAPTER I. INTRODUCTION

A. PURPOSE, SCOPE, AND ARRANGEMENT OF THE MANUAL

1. Purpose and Scope

The Redox Technical Manual has been prepared to provide a documentation of the fundamental technical bases for the process as well as a description of the general features of the Redox production facilities at Hanford Works. The manual is intended for use as a means for training and educating personnel unfamiliar with the process and as a process handbook and reference for the use of personnel responsible for the operation of the plant.

The material contained in this manual was assembled by members of the Chemical Development Section, Separations Technology Division, between September 1950 and April 1951.

2. Arrangement

The manual is divided into five parts and an appendix as follows:

Part	Title
I	Introduction
II	Process
III	Plant and Equipment
IV	Process Control
V	Safety
Appendix A	Nucleonics

Part I contains a summary of general information on the plant and process, designed to provide the reader with a synoptic view as an aid in understanding the subsequent parts.

Part II contains a step-by-step description of the process with statements and discussions of the scientific and engineering principles involved, and outlines of procedure, including remedies for any off-standard conditions.

Part III describes the plant layout, equipment arrangement, and individual equipment pieces.

Part IV describes the instruments and analytical methods used for process control.

Part V describes process hazards and the methods used to safeguard against them.

The appendix contains some nucleonics background information, designed to help orient the reader in this comparatively new field.

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Each part contains one or more chapters. A total of twenty-five chapters is included in the five parts. Pages are numbered to designate the chapter number (i.e., Chapter I page numbers begin with 101, Chapter II with 201, etc.). A table of contents is listed on the first page of each chapter. Figures and tables are located at the end of each chapter and are numbered in one series for each chapter (e.g., Table I-1, Figure I-2, Figure I-3, etc.). References to material containing more detailed information on specific points are listed at the end of each chapter, just before the figures and tables.

A subject index, in alphabetical order, is included in the back of the manual for quick reference to specific points.

B. FUNCTION OF THE PLANT

1. Design Basis

The function of the Redox Plant is the recovery of plutonium and uranium from uranium slugs irradiated in the Hanford piles. The function involves the separation of plutonium and uranium from each other and from the radioactive fission products formed in the slugs. This is accomplished by a solvent-extraction process.

The plant is designed for an average uranium production rate of 1 to 2.5 short tons per day and an average plutonium production rate of 634 grams per day. The maximum instantaneous production rates used as the design basis are based on an assumed 80% operating time efficiency, i.e., 20% down time for repairs, maintenance, etc. Thus the maximum instantaneous design production capacities are 3.125 short tons per day for uranium and 791 grams per day for plutonium. Actual instantaneous plutonium production rates as high as 1200 grams per day (at uranium production rates of up to 3.125 short tons per day) may be attainable with minor modifications of operating procedure; and rates as high as 4 tons of uranium and 1500 grams of plutonium per day may be attainable with some relatively minor equipment revisions.(1)(2)

The plant is designed to recover at least 98 to 99% of the plutonium and uranium in the irradiated slugs processed.

2. Feed Material

The feed to the Redox Plant consists of irradiated uranium slugs from the Hanford piles. The slugs are uranium cylinders 4.00 inches long and 1.36 inches in diameter, encased in thin aluminum jackets or "cans". Between discharge from the piles and entry into the Redox Plant these slugs are stored for about 40 to 90 days to permit "cooling", i.e., radioactive decay of fission products. As received in the Redox Plant the irradiated slugs have a plutonium content of about 380 to 530 grams per short ton of uranium depending on the number of megawatt-days of pile irradiation received by the slugs. The beta radioactivity due to fission products in the slugs is 0.1 to 0.5 (theoretical) curies per

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gram of uranium, and the gamma radioactivity 0.07 to 0.4 curies per gram. The exact specific radioactivity of the slugs is a function of their irradiation and "cooling" history. The specific beta and gamma radioactivities of slugs irradiated at 400 megawatts for 250 days and then "cooled" for 90 days are respectively 0.14 and 0.10 (theoretical) curies per gram of uranium. The slugs are described and discussed in greater detail in Chapter II.

3. Plutonium Product

The final plutonium product of the Redox Plant is a plutonium nitrate solution containing approximately 10 grams of plutonium per liter and 400 to 600 grams per liter of free nitric acid. The maximum uranium and radioactive fission-product concentrations in the recovered plutonium solution, while not firmly established at the time of this writing, are expected to be approximately as follows:

Uranium	0.1 weight per cent of the Pu metal
Beta plus gamma radioactivity from fission products	8×10^{-5} (theoretical) curies/g. Pu

The concentration of non-radioactive impurities in the plutonium is expected to be low, the principal impurities being aluminum and iron (about 30,000 and 10,000 parts per million parts of Pu, respectively). The composition of the final plutonium product is discussed in detail in Chapter VII. Firm chemical purity specifications for the plutonium product have not been established at the time of this writing, but an appraisal of present purity requirements plus expected impurity removal in subsequent processing steps indicates that the final product will be satisfactory.

4. Uranium Product

The uranium product of the Redox Plant is a concentrated uranyl nitrate solution containing approximately 1004 grams of uranyl nitrate hexahydrate per liter, i.e., 476 g. U/l. At the time of this writing it is tentatively expected that the specifications for the maximum plutonium and radioactive fission-product concentrations in the recovered uranium solution will be approximately as follows:

Pu	10 parts per billion parts of U (This is the expected plant performance, as opposed to 100 parts per billion given below for tentative specifications for UO_3.)
Beta radioactivity	1×10^{-7} (theoretical) curies/g. U (30% of natural uranium beta)
Gamma radioactivity	5×10^{-8} (theoretical) curies/g. U (300% of natural uranium gamma)

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The three uranium decontamination cycles will probably reduce the radioactivity in the recovered uranium solution to approximately 10 per cent and 100 per cent of the natural uranium beta and gamma activity respectively.

The principal non-radioactive impurities in the uranium product of the Redox Plant are as follows:

Impurity	Approximate Concentration, Parts per Million Parts of U
HNO_3	10,000
Sodium	400
Aluminum	600
Iron	150

The uranyl nitrate solution constituting the final uranium product of the Redox Plant is part of the feed to the Uranium Conversion Plant (224-U Building), where the uranyl nitrate is calcined to uranium trioxide (UO_3). Tentative specifications for the UO_3 product are as follows:

Constituent or Property	Tentative Specification*
Beta activity from fission products	not to exceed 30% of natural uranium
Gamma activity from fission products	not to exceed 300% of natural uranium
Pu content	not to exceed 100 p.p.b.
UO_3 content	not less than 97% by wt.
Sodium content	not to exceed 1000 p.p.m.
Phosphate content	not to exceed 2000 p.p.m.
Iron content	not to exceed 1000 p.p.m.
S, Mo, Cr, W, Si, B, Ni	not to exceed 100 p.p.m. each
Water content	not to exceed 0.1%
Nitric acid content	not to exceed 0.6%
Particle size	80% through 80 mesh
Bulk density	not less than 3.2 g./ml.

* These specifications are at this writing subject to considerable uncertainty.

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14

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C. PRINCIPLES AND OUTLINE OF THE REDOX PROCESS

The Redox process is designed to separate uranium and plutonium as product streams from the fission products with which they are associated in irradiated uranium slugs. The process is one of solvent-extraction, in which the components are separated from one another by controlling their relative distribution between aqueous solutions and the immicible organic solvent, hexone (methyl isobutyl ketone). In the following sub-sections the basic principles of the process are briefly explained and the several steps which make up the process are outlined. This section is intended only as an introduction to the process, more complete information being contained in Part II (Chapters II through X).

1. Basic Principles

1.1 Properties of uranium of process importance

The Redox process utilizes the preferential extractability of uranyl nitrate by hexone to separate uranium from plutonium and the fission-product elements.

Metallic uranium is soluble in nitric acid to form solutions of $UO_2(NO_3)_2$. A fast dissolution rate is favored by high concentrations of nitric acid and high temperatures.

The salts of uranium consist chiefly of two classes: (a) the uranous, U(IV), green in color; and (b) the uranyl, UO_2^{+2}, yellow in color with a strong greenish fluorescence. Uranium is capable of existing in other valence states, but only the tetravalent and hexavalent are comparatively stable in aqueous solutions. U(IV) is a strong reducing agent; it therefore follows that it is difficult to reduce UO_2^{+2} to U(IV). $UO_2(NO_3)_2$, the product of uranium metal dissolution in nitric acid, is very soluble in aqueous solutions and in hexone. When aqueous solutions of uranyl nitrate are contacted with hexone, the uranium can be made to distribute preferentially into the organic phase by adding a salting agent, aluminum nitrate, to the aqueous phase. This preferential distribution and the relative non-reducibility of UO_2^{+2} make possible the separation of uranium from plutonium and the fission products in the Redox process.

1.2 Properties of plutonium of process importance

The Redox process utilizes the preferential extractability of the plutonium(IV) and (VI) nitrates by hexone and the virtual non-extractability of plutonium(III) nitrate to separate plutonium from uranium and the fission-product elements.

The metal solution resulting from the dissolution of irradiated uranium slugs in nitric acid contains plutonium with the (IV) valence state prevailing.

Solutions of trivalent (blue-violet), tetravalent (brown-green), pentavalent (colorless), and hexavalent (pink-orange) plutonium have been

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produced. Pu(V) is unstable, and soon disappears by disproportionation to other valence states. Pu(III) is more stable than Pu(V) but in the presence of air or other oxidants is rather easily converted to Pu(IV). Both the Pu(IV) and (VI) nitrates can be made to distribute preferentially from an aqueous solution salted with aluminum nitrate into hexone in the same manner as $UO_2(NO_3)_2$, while the Pu(III) nitrate always favors the aqueous phase. This solvent-extractability of the IV and VI valence states makes possible the separation of plutonium from the fission products while the relatively easy reduction of plutonium to the virtually non-extractable III valence state makes possible the separation of plutonium and uranium in the Redox process.

1.3 Properties of the fission products of process importance

The relative non-extractability of the fission-product elements by hexone makes possible their separation from uranium and plutonium in the Redox process.

Fission-product elements important in plant operations are listed in Chapter II. Some of these fission products (I, Xe, Kr, and others present in smaller quantities) are gaseous and are for the most part evolved in the dissolution of the pile metal. The fission products remaining in the metal solution are, in general, relatively inextractable into hexone, even when the aqueous phase contains a salting agent, and thus largely remain in the aqueous phase at the conditions under which plutonium and uranium are extracted.

One fission product, ruthenium, has been found often to limit the decontamination of uranium that may be realized by solvent-extraction methods. Ruthenium may be oxidized by $KMnO_4$ or ozone to the tetroxide (RuO_4), which is volatile and may be removed from the metal solution by sparging the solution with a carrier gas (e.g., air). Two other fission products, zirconium and niobium (columbium), are almost quantitatively adsorbed on precipitated MnO_2 formed by the reduction of $KMnO_4$ and on certain filter-aids. Other fission products are also adsorbed, to a lesser extent, in this manner. In order to improve decontamination and thus possibly eliminate the need for one or more solvent-extraction cycles, equipment for ruthenium distillation and zirconium-niobium scavenging has been incorporated in the Redox Plant feed preparation facilities.

1.4 Decontamination

As shown on the HW #4 Redox Plant Chemical Flowsheet (Fig. I-2), the beta and gamma-emitting fission products associated with irradiated uranium slugs exposed for 400 megawatt-days/ton are reduced by factors of 2.3×10^6 and 1.5×10^6, respectively, for uranium and 5×10^6 and 1×10^7, respectively, for plutonium in the solvent-extraction cycles of the Redox process. The factor by which the concentration of radioactive contaminants is reduced is termed the "decontamination factor" (D.F.), which can be expressed mathematically as follows:

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$$D.F. = \frac{\text{Radioactivity initially present}}{\text{Radioactivity present at step in question}}$$

Either the gamma or beta radiations may be used as an index of the fission-product radioactivity present, and the decontamination factor thus determined is called the "gamma D.F." or "beta D.F.". A logarithmic method of expressing decontamination factors is also used, and is related to the D.F. by the following expression:

$$dF = \log_{10} (D.F.)$$

Therefore, a D.F. of 10^5 is equivalent to a dF of 5, D.F. of 20 equals dF of 1.3, etc.

1.5 Simplified flowsheet

Figure I-1 is a simplified flowsheet of the Redox process including the feed preparation, solvent-extraction, solvent treatment, and waste treatment steps. Individual parts of the process are discussed in the subsections following.

This flowsheet shows the code letters usually used to identify the solvent-extraction column influent and effluent streams in the Redox process, such as IAX, 2BP, 3EW, etc. The first two letters of this code identify the solvent-extraction column. The last letter identifies the stream. Influent stream abbreviations end in F, X, or S, which stand for feed (uranium or plutonium), extractant, and scrub, respectively. Effluent stream abbreviations end in P, U, or W, which stand for plutonium, uranium, and waste, respectively. Effluent streams containing both uranium and plutonium end only in P. Thus the IAP stream is the effluent stream from the IA Column containing both uranium and plutonium.

2. Feed Preparation

The purpose of the feed-preparation process is to prepare a solution from pile-irradiated uranium slugs for feed to the First Solvent-Extraction Cycle.

The feed preparation process includes the following steps:

(a) The aluminum jackets are removed from the irradiated slugs by a solution containing 10% sodium hydroxide and 20% sodium nitrate, at boiling temperature. The resultant coating removal waste is sent to underground storage tanks.

(b) The uranium slugs, containing plutonium and fission products, are then dissolved in 60 per cent nitric acid at boiling temperature. The off-gas formed in the dissolution is passed through a "silver reactor" where, by reaction with silver nitrate, the highly toxic radioactive iodine is effectively removed.

(c) The metal solution from the dissolving step is treated, at near-boiling temperatures, with sodium dichromate, which

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oxidizes the plutonium to the VI valence state. The solution may be further treated with potassium permanganate to oxidize the radio ruthenium to the volatile tetroxide, which may be swept from the solution by sparging with air. The ruthenium is then removed from the off-gas in a caustic scrubbing column. Bottoms from this column are routed to underground storage tanks.

(d) After oxidation, the metal solution is centrifuged to remove any solid material which may be detrimental to the performance of the solvent-extraction columns. Before centrifugation the solution may be scavenged with Super Filtrol (a filter-aid) or a co-formed manganese dioxide precipitate. Zirconium and niobium fission products are largely adsorbed on these scavenging agents and thus removed during centrifugation. The Super Filtrol is added to the solution as a slurry, while manganese dioxide is formed by reducing potassium permanganate (added during oxidation) with chromic nitrate or manganous nitrate. The cake from the centrifugation operation may be either slurried or dissolved out of the centrifuge bowl and is disposed of to underground storage tanks.

(e) The final adjustment of the metal solution to a proper composition as a feed to the first solvent-extraction column (the IA Column) is made by the addition of a sodium hydroxide solution to make the feed solution appropriately acid-deficient.*

3. Solvent-Extraction

A number of modified flowsheets have been proposed for the Redox process since the development of the original flowsheet at the Argonne National Laboratory. Typical modifications are the HW #4 Flowsheet (Figure I-2); the A.N.L. June, 1948 Flowsheet (Figure I-3); and the O.R.N.L. June, 1949 Flowsheet (Figure I-4). While the HW #4 Flowsheet served as the nominal design basis for the Redox Plant, enough flexibility has been built into the plant to make it possible to operate it under a comparatively wide range of process conditions, including those of the A.N.L. and O.R.N.L. Flowsheets.

The outline presented under 3.1, 3.2, and 3.3, below, is based primarily on the HW #4 Flowsheet (Figure I-2). However, to a large extent it also applies to the A.N.L. and O.R.N.L. Flowsheets. The relative merits of the alternative flowsheets and the essential differences between them are summarized under 3.4, below.

*) An acid-deficient solution is one which would become stoichiometrically neutral upon addition of nitric acid equivalent to the deficiency (e.g., an acid-deficient solution designated as "-" 0.2 M HNO_3 would become stoichiometrically neutral upon addition of 0.2 mole of HNO_3 per liter).

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3.1 First Extraction Cycle

The First Extraction Cycle accomplishes the primary separation of the metal solution into (a) an aqueous plutonium stream, (b) an aqueous uranium stream, and (c) an aqueous stream containing the bulk of the fission-product elements.

The feed solution from the Feed Preparation Section (IAF) is continuously fed to the intermediate feed point of the IA Column. A countercurrent flow of acidified hexone (IAX) extracts uranium and plutonium, both in the VI valence state, from the aqueous phase into the organic in the presence of a salting agent, aluminum nitrate, introduced in an acid deficient aqueous solution (IAS) at the top of the column. In this manner, uranium and plutonium in the organic phase are separated from the bulk of the fission-product elements which are carried into the aqueous effluent.

The organic overhead (IAP-IBF) containing uranium and plutonium is contacted in the IB Column with a countercurrent flow of slightly acidified aqueous solution (IBX) containing ferrous sulfamate and aluminum nitrate. The ferrous sulfamate reduces plutonium to the III valence state, thus permitting it to be extracted into the aqueous phase while uranium continues to favor the organic phase. The aqueous phase is scrubbed of any uranium by slightly acidified hexone (IBS) introduced at the bottom of the column. The aqueous plutonium stream (IBP) is further decontaminated in the Second and Third Plutonium Cycles.

The uranium in the organic stream from the IB Column (IBU-ICF) is transferred into the aqueous phase in the IC Column by countercurrent extraction with an aqueous stream. The aqueous effluent (ICU) is then stripped of dissolved hexone, concentrated, and simultaneously adjusted to the required acid-deficiency in the ICU Concentrator. This concentrated uranium stream constitutes the feed to the Second and Third Uranium Cycles.

3.2 Second and Third Uranium Cycles

The Second and Third Uranium Cycles further decontaminate the uranium from residual traces of radioactive fission products and plutonium which carry over with the uranium from the First Extraction Cycle.

The aqueous uranium concentrate (2DF) from the First Extraction Cycle is fed to the intermediate feed point of the 2D Column. This unit is operated in the same manner as the IA Column described above. The feed stream is contacted with a countercurrent flow of acidified hexone (2DX) and scrubbed with an aqueous acid-deficient aluminum nitrate-ferrous sulfamate solution (2DS). The uranium transfers into the hexone phase and is carried overhead while traces of fission-product elements and plutonium leave the bottom of the column in an aqueous stream (2DW).

The uranium-bearing hexone stream (2DU-2EF) flows directly to the bottom of the 2E Column, where, just as in the IC Column described above, uranium is transferred back into the aqueous phase by countercurrent extraction with an aqueous stream (2EX).

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Again, as in the ICU concentration described above, the 2E uranium stream (2EU) is stripped, concentrated, and adjusted to the required acid-deficiency. The concentrated solution (3DF) may then be fed to the Third Uranium Cycle if further decontamination is required.

The Third Uranium Cycle serves to decontaminate the uranium solution still further from residual traces of the fission-product elements and plutonium and is identical with the Second Uranium Cycle except that partial neutralization in the final concentrator is not required. The final concentrated uranyl nitrate solution is shipped to the Uranium Conversion Plant for calcination to uranium trioxide (UO_3) before shipment off-site. Ruthenium, zirconium, and niobium decontamination procedures in the Feed Preparation Step, discussed in Subsection 2, above, may make operation of the Third Uranium Cycle unnecessary.

3.3 Second and Third Plutonium Cycles

The function of the Second and Third Plutonium Cycles is to decontaminate the plutonium adequately from residual traces of the fission-product elements which carry over from the First Extraction Cycle.

The aqueous effluent from the IB Column (IBP) contains plutonium in the III valence state. The solution is oxidized by the addition of nitric acid and sodium dichromate to place plutonium in the IV or VI valence state so that it may be extracted with hexone and thus further decontaminated. The oxidized solution (2AF) is fed to the center feed point of the 2A Column.

The 2A and 2B Columns as well as the 3A and 3B Columns are operated in the same manner as the 2D, 2E, 3D, and 3E Columns in the Second and Third Uranium Cycles, except that none of the column feed streams are acid-deficient and no ferrous sulfamate is added to the scrub streams. The aqueous plutonium stream from the 2B Column (2BP) is adjusted to the 3A Column feed composition by adding aluminum nitrate solution. Because of its already small flow rate, the 2BP is not concentrated by boiling off water.

The aqueous plutonium stream from the 3B Column (3BP) is concentrated for shipment to (231 or) 234-5 Building.

3.4 Alternative flowsheets

The HW #4 Flowsheet (Figure I-2), upon which the outline above was primarily based, is only one of the modifications of the Redox process upon which the Redox Plant may be operated. The A.N.L. June, 1948 Flowsheet (Figure I-3) and the O.R.N.L. June, 1949 Flowsheet (Figure I-4) represent other feasible modifications. The essential differences between these alternative flowsheets are in the nitric acid concentrations in the entering streams and in the aluminum nitrate concentrations in the scrub streams to the uranium decontamination columns (the 1A, 2D, and 3D Columns). The differences are summarized in the following table:

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Concentrations in the IA, 2D, and 3D Column Feed Streams

Flowsheet	Aluminum Nitrates, M	Nitric Acid, M		
	Scrub	Feed	Scrub	Extractant
HW #4	1.8	-0.2	-0.2	+0.2
A.N.L. June, 1948	1.3	+0.3	0	+0.5
O.R.N.L. June, 1949	2.0	-0.2	-0.2	0

The major advantages and disadvantages of the alternative flowsheets are as follows:

Flowsheet	Advantages	Disadvantages
A.N.L. June, 1948	1. Low Pu losses 2. Most economical of aluminum nitrate	1. Low decontamination per cycle
O.R.N.L. June, 1949	1. High decontamination per cycle	1. Possibly higher Pu losses from the IA column 2. Uses the most aluminum nitrate
HW #4	1. Combines most of the advantages of O.R.N.L. and A.N.L. Flowsheets	1. Waste losses and decontamination are sensitive to minor variation in stream compositions

4. Solvent Treatment

The Organic Recovery Section reclaims used hexone for recycle to the process.

All spent hexone streams (from the IC, 2E, 3E, 2B, and 3B Columns) are fed directly from a header to a scrubber column (IO) where water or a 2% sodium carbonate solution serves to remove the bulk of the plutonium, uranium, and fission products which may be present in the hexone. The overhead from this scrubber is fed to a distillation column, in which, by distillation and contact with aqueous caustic reflux, the hexone is further decontaminated from uranium, plutonium, and fission products and purified of any methyl isopropyl diketone and organic acids (formed by decomposition of hexone) which may be present. Following this distillation the hexone may be subjected to further chemical treatment if it is still unsuitable for feed to the extraction columns because of impurities such as methyl isobutyl carbinol. Fresh hexone is also added to the process at this point. The combined fresh and recovered hexone is then recycled to the extraction columns. Acid additions to the hexone are made by continuous line blending just prior to feeding to the columns.

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5. Waste Treatment and Disposal

The function of the Waste Treatment Section is to treat and segregate according to their radioactivities the aqueous waste streams from the extraction and distillation columns and concentration vessels, and to recover dissolved hexone from these aqueous wastes.

All fission-product wastes from the 1A, 2A, 3A, 2D, 3D, IO, and Organic Distillation Columns are fed to a Waste Concentrator. The high-radioactivity bottoms from this boil-up vessel, which are concentrated (for storage volume economy) to the highest practical aluminum nitrate content, are blended with the high-radioactivity wastes from the Ruthenium Scrubber and the Laboratory Building (222-S). The resultant solution is neutralized with caustic before disposal to the mild-steel-lined underground storage tanks. To avoid rapid corrosion of these tanks at the low pH of aluminum nitrate solutions, sufficient caustic is added to convert the aluminum nitrate to sodium aluminate.

The overhead from the Waste Concentrator joins the overheads from the uranium and plutonium concentrators and flows to the Condensate Stripper where hexone is removed and sent to the Organic Recovery Section. The bottoms of this column are then evaporated before being cribbed as low-radioactivity wastes. The tailings from this evaporation are recycled to the Waste Concentrator.

Jacket removal wastes are sent directly to underground storage tanks.

6. Off-Standard Streams

Provisions have been made in the process design for reworking any off-standard streams. Rework methods are necessary for either of two possible reasons: (a) a waste stream may contain an excessive amount of uranium or plutonium, or (b) a product stream may not be sufficiently decontaminated from fission products or other impurities.

Waste streams requiring rework may be further subdivided into aqueous and organic waste streams. The former are handled in the Waste Treatment Section where they are concentrated and adjusted in composition for feeding to the IS Column. The IS Column is located in the First Extraction Cycle and is functionally identical with the IA Column, except that it is intended primarily for rework.

The organic wastes are treated in the Organic Recovery Section where any plutonium or uranium is transferred to the aqueous phase in the IO Column. The aqueous effluent from the IO Column is directed to the Waste Concentrator in the Waste Treatment Section. As before, the rework solution is sent to the IS Column.

Insufficiently-decontaminated uranium or plutonium product streams are handled in the extraction battery alone. Thus, an off-specification uranium product stream is recycled to the beginning of the Second Uranium Cycle. Similarly, an off-specification plutonium stream is recycled either to the beginning of the Second Plutonium Cycle, or, if the uranium

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content is too high, to the First Extraction Cycle for reprocessing in the IB Column.

D. THE REDOX PLANT

The Redox Plant is located in the 200 West Area of the Hanford Works, approximately thirty miles from Richland, Washington, and six miles from the nearest pile area, 100-B. A detailed map of the Hanford Works and a plot plan of the 200 West Area are contained in Chapter XI (Fig. XI-1 and XI-2, respectively). Chapters XI through XVIII of this manual contain a detailed description of the Plant and its equipment.

1. General Plant Layout

1.1 Redox Area layout

The Redox Area layout is shown on Figure I-5. This layout drawing shows the relative location of the Processing Building (202-S); the Analytical and Plant Assistance Laboratory, Building 222-S; and some of the auxiliary facilities.

The layout of the Processing Building (202-S) is discussed under 1.2, below.

The Analytical and Plant Assistance Laboratory, Building 222-S, contains laboratories for process control of Redox and other processes and a wing for chemical research and process chemistry work on a multi-curie scale.

The functions of the Processing Building auxiliary facilities are as follows:

Facility	Function
203-S Metal Storage	Storage of recovered uranium solution.
207-S Retention Basins (not shown on Fig. I-5)	Retention of exit cooling water and steam condensate before disposal to pond.
211-S Chemical Storage	Storage of 50% sodium hydroxide, 60% nitric acid, 72% aluminum nitrate, and demineralized water.
216-S Cribs (not shown on Fig. I-5)	Disposal of low-radioactivity wastes to ground.
240-S Diversion Box	Routing of process wastes to 241-S Diversion Box.
241-S Diversion Box (not shown on Fig. I-5)	Routing of process wastes to 216-S Cribs and 241-S Tank Farm.

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Facility	Function
241-S Tank Farm (not shown on Fig. I-5)	Underground storage of high-radioactivity wastes.
276-S Solvent Storage and Make-Up	Storage and pretreatment of new hexone, plus storage and retreatment of recovered hexone.
277-S Redox Mock-Up Shop (not shown in Fig. I-5)	Mock-up of cell and silo areas for fabrication of precision-fitting equipment.
291-S Ventilation Filter, Fans and Stack	Disposal of ventilation air.
291-S Process Vessel Ventilation System Jet Pit	Disposal of gaseous process wastes (filtered in 202-S Building) to stack.
Column Carrier Outlet	Removal of solvent-extraction columns from 202-S Building Silo.
Inert-Gas Generator	Generation of inert gas for blanketing of process vessels containing hexone.
2726-W Propane Storage	Storage and vaporization facilities for propane fuel burned in the inert-gas generator.

1.2 Processing Building (202-S) layout

The Redox Processing Building, 202-S, is a multistoried, predominantly reinforced concrete structure with overall dimensions of approximately 160 ft. (width), by 140 ft. (height), by 475 ft. (length). Figure I-6 is a simplified sketch of the building layout. Figure I-7 is a perspective cut-away viewed from the southwest corner of the building.

The building has two major portions: the process portion which contains the "hot" process equipment and the regulated work zones, and the service portion which houses personnel and equipment necessary for remote operation of the process portion.

The process-portion processing equipment areas are: the Silo column enclosure, the Canyon cells, and the Product Removal Cage (located at the west end of the North Sample Gallery). The Silo column enclosure houses the solvent-extraction columns. The Canyon cells house the processing equipment for dissolving slugs received from the 100-Area piles (Cells A, B, and C), preparation of feed solution suitable for the Redox process (Cell H), handling the solutions pumped to and from the solvent-extraction columns (Cells E and F), neutralization and concentration of waste solutions (Cell D), decontamination and purification of organic solvent

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(Cell G), and decontamination of process off-gases (Cell J). The Product Removal Cage houses the equipment for concentration of the plutonium product solution prior to shipment.

The regulated work zones consist of rooms and galleries where limited contact of personnel with radiation and radioactive contamination is allowed under carefully prescribed and monitored conditions. The following are regulated work zones: Canyon Deck Level, Sample Galleries, Canyon Crane Gallery, Canyon Crane Maintenance Platform, Silo Crane Level, Remote Shop, Decontamination Room, Regulated Shop, and Health Instrument Room. The SWP (regulated work) Lobby is the central point used for entrance to the regulated work zones and exit from the zones to the outside.

The service portion has rooms, shops, and equipment required for plant operation, and includes an entrance lobby, offices, lunch room, toilets, regulated change rooms, and locker rooms. The shops provided are: maintenance, instrument (industrial and electronic), and electrical. Control rooms provided are: the operating galleries on the north and south sides of the Canyon and over the Silo. Equipment rooms necessary for building operation are: blower rooms (5), a compressor room, a chemical storage room, aqueous make-up levels (5), a Silo feed gallery, electrical substation, 480-volt electrical distribution centers (2), an ozone generator room (Hivox Room), and pipe galleries (north and south).

2. Special Features of the Plant

The high levels of radiation associated with process solutions, the nature of the process materials, and the nature of the process itself have necessitated the installation of many special features, some generally used in plutonium separations plants and some peculiar only to the Redox Plant. These and other features of the plant which are of primary interest are listed below.

2.1 Continuous processing

The Redox Plant is designed to conduct processing operations on a continuous basis, except for the feed preparation and plutonium concentration steps which are batch operations. The plutonium cross-over oxidation equipment may be set up to operate either batch-wise or continuously. The continuous nature of the process requires the use of a greater variety and number of automatic control instruments than are generally provided in batch-operated plants.

2.2 Shielding

All service portions of the Processing Building must be shielded from the processing areas to prevent personnel from receiving excessive amounts of radiation. Concrete walls, of thicknesses greater than necessary for structural soundness, are used to reduce radiation intensities so that personnel in these areas will not receive radiation in excess of 0.1 mr./hr.

Inside the process portions, the regulated work zones are shielded

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from the Silo and Canyon process equipment areas by concrete walls and cell cover blocks so that radiation intensities in these zones are normally less than 1 mr./hr.

Materials other than concrete which are used for shielding inside the building are lead glass (for viewing windows) and steel.

Outside sources of radiation (waste piping, waste tanks, and the railroad tunnel) are shielded with earth cover and/or concrete.

2.3 Remote operation

Location of the process equipment behind massive concrete shielding necessitates that this equipment be operated by remote control.

Processing operations are controlled from the operating galleries except for the Dissolver charging operation which is accomplished with the aid of the Canyon Crane (described under 2.4, below). Some of the methods and devices employed for remote operation are briefly described below.

Irradiated uranium slugs are brought into the Processing Building via the railroad tunnel on special cars. They are then charged to the Dissolvers with the Canyon Crane. Chemical additions to the process vessels are made from the service areas through pipe lines running through the concrete shielding. Solution transfers between vessels are made by means of steam jets and, in cases where the flow rate must be closely controlled, by electrically operated pumps submerged in the process solutions. Flow rates of these pumped streams are controlled from the operating galleries by recording-controlling instruments which receive an impulse indicating the flow rate from a transmitting rotameter and in turn actuate an air-operated valve. Agitation of the vessel solutions is accomplished with remotely-operated recirculating steam jets or electrically driven agitators. The hexone-aqueous interface levels in the solvent-extraction columns are controlled by recorder-controller instruments which are actuated by inert-gas bubbling dip tubes located in the column tops. The controller then maintains the interface level by adjusting an air-operated control valve in the aqueous stream leaving the column. Indications of the total weight and specific gravity of solutions are read from differential-pressure instruments actuated by bubbler dip tubes in the vessels. Solutions are sampled via vacuum jets which draw the solutions into shielded sample boxes in the sample galleries.

2.4 Remote maintenance

Installation and removal of process equipment, and servicing operations in both the Canyon and Silo, are accomplished with the aid of cranes. The Canyon Crane (60-ton) is operated from a steel-shielded control cab which travels behind the concrete wall of the Crane Cab Gallery. Operations are observed from the cab through periscopes. The Silo Crane (10-ton) may be operated from its steel-shielded cab or from any of seventeen remote control stations located at various levels along

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the north and west walls of the column enclosure. Operations may be viewed through any of the lead-glass viewing windows which are located in the cab as well as at strategic positions in the Silo wall next to remote control stations for operating the crane.

All Canyon and Silo equipment pieces may be removed with the cranes. All equipment pieces are fastened in place with enlarged nuts which may be tightened or loosened with a crane-operated impact wrench. Piping, electrical, and auxiliary connections are made with special connectors which may be tightened or loosened by rotating a single nut with the impact wrench. Each large equipment piece is provided with bails so that it may be lifted with a crane hook.

Columns are placed in a special carrier container before removal from the Silo. This container is then removed through an underground tunnel to the Column Carrier Outlet. Replacement columns are brought into the building in the same manner.

Canyon equipment in need of repair is carried to the maintenance facilities at the east end of the Canyon. The equipment may be partially decontaminated and disassembled in the Remote Shop. It may then be decontaminated further in the Decontamination Room and brought into the Regulated Shop for contact maintenance, if necessary. Equipment to be replaced is boxed up and removed from the Processing Building through the Railroad Tunnel.

2.5 Silo structure

The length of the solvent-extraction columns (58 ft. maximum) and the locating of some of their auxiliary equipment above them has made necessary the construction of a special portion of the building known as the Silo. The Silo is approximately 132 ft. high, 84 ft. long, and 40 ft. wide. The Silo roof is approximately 140 ft. higher than the building base line, 52 ft. higher than the Canyon roof, and 120 ft. above grade level.

Located in the Silo are the column enclosure (84 ft. high), facilities for aqueous make-up, tanks for feeding "cold" (non-radioactive) feed streams to the columns by gravity flow, facilities for sampling column streams, a 10-ton crane, and the column operating center.

2.6 Materials of construction -- equipment

The corrosive nature of the solutions processed in the Redox Plant (primarily nitric acid of various concentrations) requires the use of stainless-steel vessels and lines for the handling of the process liquids and gases. All vessels in the process areas are constructed of 18-8 stabilized stainless steel, except those normally operated at high temperatures which are constructed of 25-12 Cb stabilized stainless steel. The construction materials of the vessels in the service areas are usually stainless or mild steels, depending upon the nature of the solutions which they handle. Other materials are sometimes used in special cases.

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2.7 Protective coverings

Concrete is easily damaged by process solutions and tends to absorb radioactive contamination. For this reason, concrete surfaces which could possibly come in contact with process solutions are protected with a coating of acid-resistant paint or covered with stainless steel. Amercoat paints are generally used throughout the Canyon cells and in the column enclosure area. Because hexone attacks the paint, stainless steel coverings are used on the floors of the column enclosure and solvent-handling cells which may possibly come in contact with hexone. The PR Cage floor is also lined with stainless steel, as recovery of spills in this area may be necessary.

3. Safety Features of the Plant

3.1 Critical mass control

Plutonium is capable of a nuclear fission chain reaction if more than a certain critical amount (called the "critical mass") is accumulated in one place. The size of the critical mass is a function of chemical and geometric conditions as discussed in Chapter XXV.

All process vessels in the Redox Plant except those tanks which handle uranium-free plutonium (the tanks of the Second and Third Plutonium Cycles) are safe from the accumulation of a critical mass because of the nature of the solutions processed or the vessel geometry. In the Plutonium-Cycle tanks, criticality is impossible as long as each vessel contains less than approximately 0.6 Kg. of plutonium. (Even with 0.6 Kg. present, a chain reaction will not take place unless several unlikely conditions also prevail.) The plutonium processed through these tanks is normally handled in 300-gram critically-safe batches. Batch sizes are controlled by volume and by sampling. As an additional safeguard, tanks which continuously receive plutonium solution are operated so that they will overflow before receiving a volume of solution which normally would contain over 600 grams of plutonium.

3.2 Process area ventilation

To prevent the spread of radioactive contamination and solvent vapors through the air, process vessels are maintained under a negative differential pressure with respect to the cells. All process vessels are vented through Fiberglas filters and are maintained under a vacuum of from 5 to 30 inches of water. The vacuum is drawn by jets which discharge to the stack. Solvent-containing vessels are vented to an inert-gas system, while other vessels are vented to an air system.

To prevent the spread of any radioactive contamination and solvent vapor in the event of a leak from the process vessels, the Processing Building ventilation is so designed that the processing areas are maintained under a negative differential pressure (approximately 0.4 in. of water) with respect to other portions of the building.

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Ventilation air is fed to the process areas from the No. 1 Blower Room.

Air enters the Canyon and Silo process areas at the upper levels. This air is then drawn down past the process equipment, through the ventilation tunnel, and through the sand filter (where radioactive particles are removed) by the 291-S Fans. These fans discharge the air through the stack to the atmosphere.

Air fed to the Regulated Shop, Decontamination Room, SWP Lobby, H.I. Storage, and the North and South Sample Galleries is exhausted through fans to the atmosphere. The PR Cage is maintained at a negative differential pressure (approximately 0.1 in. of water) with respect to the North Sample Gallery with an individual exhaust fan. This fan draws air from the gallery into the cage and then through a replaceable filter before exhausting to the atmosphere.

3.3 Fire and explosion protection

The Redox process employs a flammable organic solvent, hexone, the vapor of which is explosive when mixed with air within the limits of 1.34 and 8.00 per cent by volume at room temperature.

A number of protective features for the prevention of fire and/or explosion have been incorporated into the Redox Plant. Among these are inert-gas blanketing of solvent-containing vessels, adequate process area ventilation, and use of explosion-proof electrical equipment in solvent areas. Despite the remoteness of the possibility of a fire and/or explosion, fire detection and water-fog fire-control systems have also been incorporated in the plant.

Details on fire and explosion safety of the Plant may be found in Chapter XXIV.

4. Chemical and Utility Requirements

The estimated chemical and utility requirements for processing 3.125 short tons of uranium per day are presented in Table I-8. Chemical requirements for ruthenium distillation and zirconium-niobium scavenging steps have not been included, because of the uncertainty, at this writing, of the exact procedure to be used for these steps.

5. In-Process Inventory

The continuous nature of the processing operations in the Redox Plant complicates the accounting of plutonium and uranium in the process equipment. Table I-9 lists the estimated in-process holdup of these materials when the Plant is processing 3.125 short tons of uranium per day, containing 400 grams of plutonium per short ton.

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REFERENCES

(1) HW-20222 Increase in Redox Capacity (Part I - Increase in Column Packing Size). R. B. Richards. 2-6-51.

(2) HDC-1956 Evaluation of Potential Capacity of Redox Production Plant -- 202-S. R. E. Tomlinson. 11-29-50.

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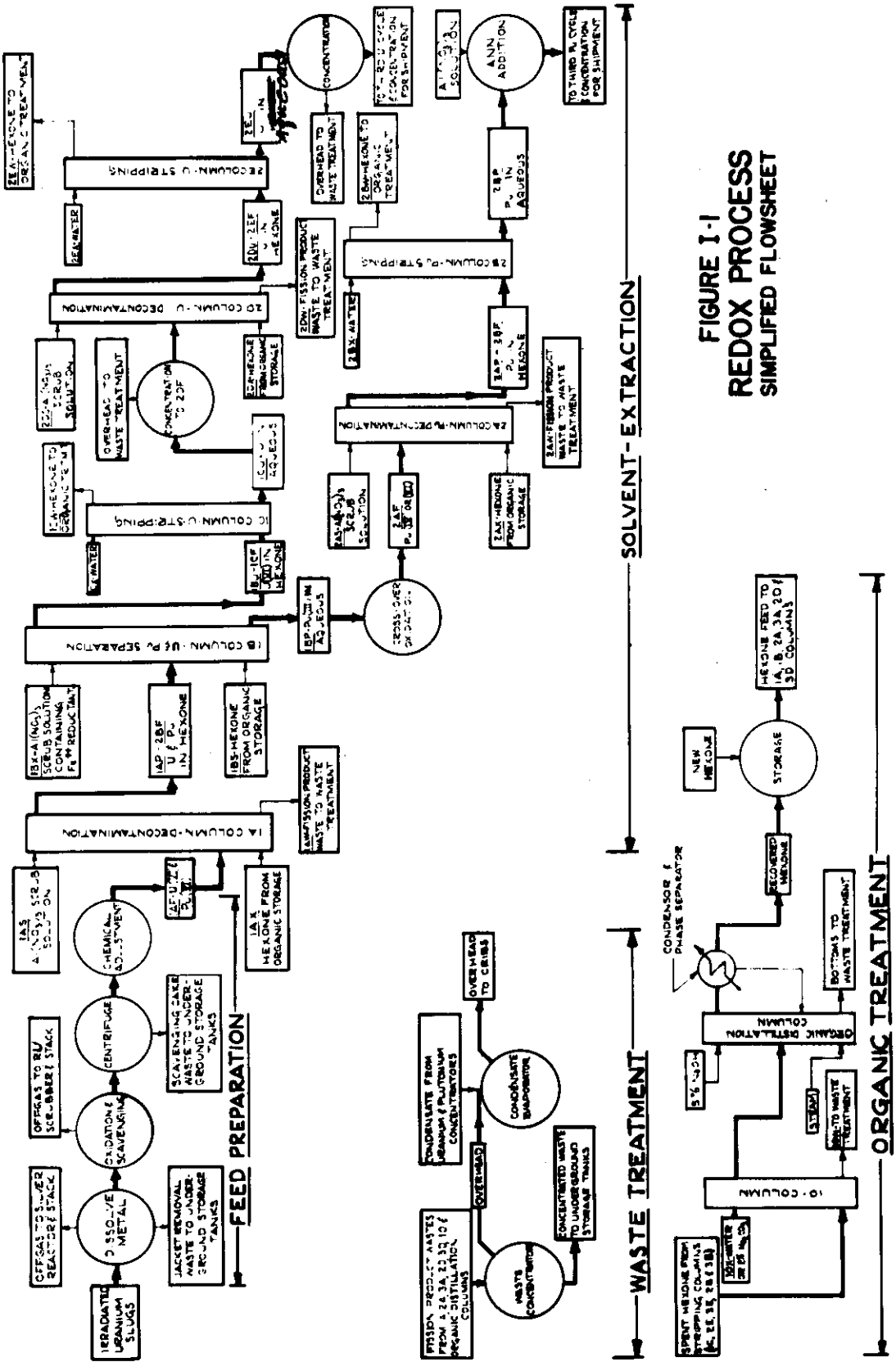
IRRADIATED URANIUM SLUGS
DISSOLVE METAL
OFFGAS TO SUMMER REACTOR 2 STACK
OFFGAS TO RU SCRUBBER 2 STACK
OXIDATION & SCAVENGING
CENTRIFUGE
JACKET REMOVAL WASTE TO UNDERGROUND STORAGE TANKS
SCAVENGING CAKE WASTE TO UNDERGROUND STORAGE TANKS
CHEMICAL ADJUSTMENT
1A5 ALUMINUM SCRUB SOLUTION
1A FEED
1A1 HEXONE FROM ORGANIC STORAGE
1A COLUMN - DECONTAMINATION
1A5 FISSION PRODUCT WASTE TO WASTE TREATMENT
1B5 HEXONE FROM ORGANIC STORAGE
1AP - 2BF U, Pu IN HEXONE
1B5 HAN(NO3)3 SCRUB SOLUTION CONTAINING Fe++ REDUCTANT
1B COLUMN - U & Pu SEPARATION
1BP - 1DF U IN HEXONE
1B W WATER
1C COLUMN - U STRIPPING
1C5 HEXONE TO ORGANIC STORAGE
1C5 ALUMINUM SCRUB SOLUTION
1C5 HEXONE FROM ORGANIC STORAGE
1CP - 2DF U IN HEXONE
1C W WATER
2D COLUMN - U DECONTAMINATION
2D5 HEXONE TO ORGANIC STORAGE
2DW FISSION PRODUCT WASTE TO WASTE TREATMENT
2DP - 2EF U IN HEXONE
2E COLUMN - U STRIPPING
2E W WATER
2EP - 2FF U IN AQUEOUS
2E5 HEXONE TO ORGANIC TREATMENT
2E5 HEXONE TO ORGANIC TREATMENT
2F COLUMN - Pu DECONTAMINATION
2FW FISSION PRODUCT WASTE TO WASTE TREATMENT
2F5 HEXONE FROM ORGANIC STORAGE
2FP - 3BF Pu IN HEXONE
2F W WATER
3B COLUMN - Pu STRIPPING
3BP - 3DF Pu IN AQUEOUS
3D COLUMN - Pu DECONTAMINATION
3DW FISSION PRODUCT WASTE TO WASTE TREATMENT
3D5 HEXONE TO ORGANIC STORAGE
3DP - 3EF Pu IN HEXONE
3E COLUMN - Pu CONCENTRATION
3EP - 3FF Pu IN AQUEOUS
3E5 HEXONE TO ORGANIC TREATMENT
3E W WATER
3E5 HEXONE TO ORGANIC TREATMENT
3F COLUMN - Pu DECONTAMINATION
3FW FISSION PRODUCT WASTE TO WASTE TREATMENT
3F5 HEXONE FROM ORGANIC STORAGE
3FP - 4BF Pu IN HEXONE
3F W WATER
4B COLUMN - Pu STRIPPING
4BP - 4DF Pu IN AQUEOUS
4D COLUMN - Pu DECONTAMINATION
4DW FISSION PRODUCT WASTE TO WASTE TREATMENT
4D5 HEXONE TO ORGANIC STORAGE
4DP - 4EF Pu IN HEXONE
4E COLUMN - Pu CONCENTRATION
4EP - 4FF Pu IN AQUEOUS
4E5 HEXONE TO ORGANIC TREATMENT
4E W WATER
4E5 HEXONE TO ORGANIC TREATMENT
4F COLUMN - Pu DECONTAMINATION
4FW FISSION PRODUCT WASTE TO WASTE TREATMENT
4F5 HEXONE FROM ORGANIC STORAGE
4FP - 5BF Pu IN HEXONE
4F W WATER
5B COLUMN - Pu STRIPPING
5BP - 5DF Pu IN AQUEOUS
5D COLUMN - Pu DECONTAMINATION
5DW FISSION PRODUCT WASTE TO WASTE TREATMENT
5D5 HEXONE TO ORGANIC STORAGE
5DP - 5EF Pu IN HEXONE
5E COLUMN - Pu CONCENTRATION
5EP - 5FF Pu IN AQUEOUS
5E5 HEXONE TO ORGANIC TREATMENT
5E W WATER
5E5 HEXONE TO ORGANIC TREATMENT
5F COLUMN - Pu DECONTAMINATION
5FW FISSION PRODUCT WASTE TO WASTE TREATMENT
5F5 HEXONE FROM ORGANIC STORAGE
5FP - 6BF Pu IN HEXONE
5F W WATER
6B COLUMN - Pu STRIPPING
6BP - 6DF Pu IN AQUEOUS
6D COLUMN - Pu DECONTAMINATION
6DW FISSION PRODUCT WASTE TO WASTE TREATMENT
6D5 HEXONE TO ORGANIC STORAGE
6DP - 6EF Pu IN HEXONE
6E COLUMN - Pu CONCENTRATION
6EP - 6FF Pu IN AQUEOUS
6E5 HEXONE TO ORGANIC TREATMENT
6E W WATER
6E5 HEXONE TO ORGANIC TREATMENT
6F COLUMN - Pu DECONTAMINATION
6FW FISSION PRODUCT WASTE TO WASTE TREATMENT
6F5 HEXONE FROM ORGANIC STORAGE
6FP - 7BF Pu IN HEXONE
6F W WATER
7B COLUMN - Pu STRIPPING
7BP - 7DF Pu IN AQUEOUS
7D COLUMN - Pu DECONTAMINATION
7DW FISSION PRODUCT WASTE TO WASTE TREATMENT
7D5 HEXONE TO ORGANIC STORAGE
7DP - 7EF Pu IN HEXONE
7E COLUMN - Pu CONCENTRATION
7EP - 7FF Pu IN AQUEOUS
7E5 HEXONE TO ORGANIC TREATMENT
7E W WATER
7E5 HEXONE TO ORGANIC TREATMENT
7F COLUMN - Pu DECONTAMINATION
7FW FISSION PRODUCT WASTE TO WASTE TREATMENT
7F5 HEXONE FROM ORGANIC STORAGE
7FP - 8BF Pu IN HEXONE
7F W WATER
8B COLUMN - Pu STRIPPING
8BP - 8DF Pu IN AQUEOUS
8D COLUMN - Pu DECONTAMINATION
8DW FISSION PRODUCT WASTE TO WASTE TREATMENT
8D5 HEXONE TO ORGANIC STORAGE
8DP - 8EF Pu IN HEXONE
8E COLUMN - Pu CONCENTRATION
8EP - 8FF Pu IN AQUEOUS
8E5 HEXONE TO ORGANIC TREATMENT
8E W WATER
8E5 HEXONE TO ORGANIC TREATMENT
8F COLUMN - Pu DECONTAMINATION
8FW FISSION PRODUCT WASTE TO WASTE TREATMENT
8F5 HEXONE FROM ORGANIC STORAGE
8FP - 9BF Pu IN HEXONE
8F W WATER
9B COLUMN - Pu STRIPPING
9BP - 9DF Pu IN AQUEOUS
9D COLUMN - Pu DECONTAMINATION
9DW FISSION PRODUCT WASTE TO WASTE TREATMENT
9D5 HEXONE TO ORGANIC STORAGE
9DP - 9EF Pu IN HEXONE
9E COLUMN - Pu CONCENTRATION
9EP - 9FF Pu IN AQUEOUS
9E5 HEXONE TO ORGANIC TREATMENT
9E W WATER
9E5 HEXONE TO ORGANIC TREATMENT
9F COLUMN - Pu DECONTAMINATION
9FW FISSION PRODUCT WASTE TO WASTE TREATMENT
9F5 HEXONE FROM ORGANIC STORAGE
9FP - 10BF Pu IN HEXONE
9F W WATER
10B COLUMN - Pu STRIPPING
10BP - 10DF Pu IN AQUEOUS
10D COLUMN - Pu DECONTAMINATION
10DW FISSION PRODUCT WASTE TO WASTE TREATMENT
10D5 HEXONE TO ORGANIC STORAGE
10DP - 10EF Pu IN HEXONE
10E COLUMN - Pu CONCENTRATION
10EP - 10FF Pu IN AQUEOUS
10E5 HEXONE TO ORGANIC TREATMENT
10E W WATER
10E5 HEXONE TO ORGANIC TREATMENT
10F COLUMN - Pu DECONTAMINATION
10FW FISSION PRODUCT WASTE TO WASTE TREATMENT
10F5 HEXONE FROM ORGANIC STORAGE
10FP - 11BF Pu IN HEXONE
10F W WATER
11B COLUMN - Pu STRIPPING
11BP - 11DF Pu IN AQUEOUS
11D COLUMN - Pu DECONTAMINATION
11DW FISSION PRODUCT WASTE TO WASTE TREATMENT
11D5 HEXONE TO ORGANIC STORAGE
11DP - 11EF Pu IN HEXONE
11E COLUMN - Pu CONCENTRATION
11EP - 11FF Pu IN AQUEOUS
11E5 HEXONE TO ORGANIC TREATMENT
11E W WATER
11E5 HEXONE TO ORGANIC TREATMENT
11F COLUMN - Pu DECONTAMINATION
11FW FISSION PRODUCT WASTE TO WASTE TREATMENT
11F5 HEXONE FROM ORGANIC STORAGE
11FP - 12BF Pu IN HEXONE
11F W WATER
12B COLUMN - Pu STRIPPING
12BP - 12DF Pu IN AQUEOUS
12D COLUMN - Pu DECONTAMINATION
12DW FISSION PRODUCT WASTE TO WASTE TREATMENT
12D5 HEXONE TO ORGANIC STORAGE
12DP - 12EF Pu IN HEXONE
12E COLUMN - Pu CONCENTRATION
12EP - 12FF Pu IN AQUEOUS
12E5 HEXONE TO ORGANIC TREATMENT
12E W WATER
12E5 HEXONE TO ORGANIC TREATMENT
12F COLUMN - Pu DECONTAMINATION
12FW FISSION PRODUCT WASTE TO WASTE TREATMENT
12F5 HEXONE FROM ORGANIC STORAGE
12FP - 13BF Pu IN HEXONE
12F W WATER
13B COLUMN - Pu STRIPPING
13BP - 13DF Pu IN AQUEOUS
13D COLUMN - Pu DECONTAMINATION
13DW FISSION PRODUCT WASTE TO WASTE TREATMENT
13D5 HEXONE TO ORGANIC STORAGE
13DP - 13EF Pu IN HEXONE
13E COLUMN - Pu CONCENTRATION
13EP - 13FF Pu IN AQUEOUS
13E5 HEXONE TO ORGANIC TREATMENT
13E W WATER
13E5 HEXONE TO ORGANIC TREATMENT
13F COLUMN - Pu DECONTAMINATION
13FW FISSION PRODUCT WASTE TO WASTE TREATMENT
13F5 HEXONE FROM ORGANIC STORAGE
13FP - 14BF Pu IN HEXONE
13F W WATER
14B COLUMN - Pu STRIPPING
14BP - 14DF Pu IN AQUEOUS
14D COLUMN - Pu DECONTAMINATION
14DW FISSION PRODUCT WASTE TO WASTE TREATMENT
14D5 HEXONE TO ORGANIC STORAGE
14DP - 14EF Pu IN HEXONE
14E COLUMN - Pu CONCENTRATION
14EP - 14FF Pu IN AQUEOUS
14E5 HEXONE TO ORGANIC TREATMENT
14E W WATER
14E5 HEXONE TO ORGANIC TREATMENT
14F COLUMN - Pu DECONTAMINATION
14FW FISSION PRODUCT WASTE TO WASTE TREATMENT
14F5 HEXONE FROM ORGANIC STORAGE
14FP - 15BF Pu IN HEXONE
14F W WATER
15B COLUMN - Pu STRIPPING
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15DW FISSION PRODUCT WASTE TO WASTE TREATMENT
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15E W WATER
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15F COLUMN - Pu DECONTAMINATION
15FW FISSION PRODUCT WASTE TO WASTE TREATMENT
15F5 HEXONE FROM ORGANIC STORAGE
15FP - 16BF Pu IN HEXONE
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16B COLUMN - Pu STRIPPING
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16D COLUMN - Pu DECONTAMINATION
16DW FISSION PRODUCT WASTE TO WASTE TREATMENT
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16EP - 16FF Pu IN AQUEOUS
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16FW FISSION PRODUCT WASTE TO WASTE TREATMENT
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16FP - 17BF Pu IN HEXONE
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17B COLUMN - Pu STRIPPING
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17DW FISSION PRODUCT WASTE TO WASTE TREATMENT
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17EP - 17FF Pu IN AQUEOUS
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17F COLUMN - Pu DECONTAMINATION
17FW FISSION PRODUCT WASTE TO WASTE TREATMENT
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17FP - 18BF Pu IN HEXONE
17F W WATER
18B COLUMN - Pu STRIPPING
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18DW FISSION PRODUCT WASTE TO WASTE TREATMENT
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19EP - 19FF Pu IN AQUEOUS
19E5 HEXONE TO ORGANIC TREATMENT
19E W WATER
19E5 HEXONE TO ORGANIC TREATMENT
19F COLUMN - Pu DECONTAMINATION
19FW FISSION PRODUCT WASTE TO WASTE TREATMENT
19F5 HEXONE FROM ORGANIC STORAGE
19FP - 20BF Pu IN HEXONE
19F W WATER
20B COLUMN - Pu STRIPPING
20BP - 20DF Pu IN AQUEOUS
20D COLUMN - Pu DECONTAMINATION
20DW FISSION PRODUCT WASTE TO WASTE TREATMENT
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20DP - 20EF Pu IN HEXONE
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20EP - 20FF Pu IN AQUEOUS
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24EP - 24FF Pu IN AQUEOUS
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24E W WATER
24E5 HEXONE TO ORGANIC TREATMENT
24F COLUMN - Pu DECONTAMINATION
24FW FISSION PRODUCT WASTE TO WASTE TREATMENT
24F5 HEXONE FROM ORGANIC STORAGE
24FP - 25BF Pu IN HEXONE
24F W WATER
25B COLUMN - Pu STRIPPING
25BP - 25DF Pu IN AQUEOUS
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25DW FISSION PRODUCT WASTE TO WASTE TREATMENT
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25E COLUMN - Pu CONCENTRATION
25EP - 25FF Pu IN AQUEOUS
25E5 HEXONE TO ORGANIC TREATMENT
25E W WATER
25E5 HEXONE TO ORGANIC TREATMENT
25F COLUMN - Pu DECONTAMINATION
25FW FISSION PRODUCT WASTE TO WASTE TREATMENT
25F5 HEXONE FROM ORGANIC STORAGE
25FP - 26BF Pu IN HEXONE
25F W WATER
26B COLUMN - Pu STRIPPING
26BP - 26DF Pu IN AQUEOUS
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26DW FISSION PRODUCT WASTE TO WASTE TREATMENT
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29F W WATER
30B COLUMN - Pu STRIPPING
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30EP - 30FF Pu IN AQUEOUS
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30F COLUMN - Pu DECONTAMINATION
30FW FISSION PRODUCT WASTE TO WASTE TREATMENT
30F5 HEXONE FROM ORGANIC STORAGE
30FP - 31BF Pu IN HEXONE
30F W WATER
31B COLUMN - Pu STRIPPING
31BP - 31DF Pu IN AQUEOUS
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31F COLUMN - Pu DECONTAMINATION
31FW FISSION PRODUCT WASTE TO WASTE TREATMENT
31F5 HEXONE FROM ORGANIC STORAGE
31FP - 32BF Pu IN HEXONE
31F W WATER
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32DW FISSION PRODUCT WASTE TO WASTE TREATMENT
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32E W WATER
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32F COLUMN - Pu DECONTAMINATION
32FW FISSION PRODUCT WASTE TO WASTE TREATMENT
32F5 HEXONE FROM ORGANIC STORAGE
32FP - 33BF Pu IN HEXONE
32F W WATER
33B COLUMN - Pu STRIPPING
33BP - 33DF Pu IN AQUEOUS
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33DW FISSION PRODUCT WASTE TO WASTE TREATMENT
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33F COLUMN - Pu DECONTAMINATION
33FW FISSION PRODUCT WASTE TO WASTE TREATMENT
33F5 HEXONE FROM ORGANIC STORAGE
33FP - 34BF Pu IN HEXONE
33F W WATER
34B COLUMN - Pu STRIPPING
34BP - 34DF Pu IN AQUEOUS
34D COLUMN - Pu DECONTAMINATION
34DW FISSION PRODUCT WASTE TO WASTE TREATMENT
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34F COLUMN - Pu DECONTAMINATION
34FW FISSION PRODUCT WASTE TO WASTE TREATMENT
34F5 HEXONE FROM ORGANIC STORAGE
34FP - 35BF Pu IN HEXONE
34F W WATER
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35BP - 35DF Pu IN AQUEOUS
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35EP - 35FF Pu IN AQUEOUS
35E5 HEXONE TO ORGANIC TREATMENT
35E W WATER
35E5 HEXONE TO ORGANIC TREATMENT
35F COLUMN - Pu DECONTAMINATION
35FW FISSION PRODUCT WASTE TO WASTE TREATMENT
35F5 HEXONE FROM ORGANIC STORAGE
35FP - 36BF Pu IN HEXONE
35F W WATER
36B COLUMN - Pu STRIPPING
36BP - 36DF Pu IN AQUEOUS
36D COLUMN - Pu DECONTAMINATION
36DW FISSION PRODUCT WASTE TO WASTE TREATMENT
36D5 HEXONE TO ORGANIC STORAGE
36DP - 36EF Pu IN HEXONE
36E COLUMN - Pu CONCENTRATION
36EP - 36FF Pu IN AQUEOUS
36E5 HEXONE TO ORGANIC TREATMENT
36E W WATER
36E5 HEXONE TO ORGANIC TREATMENT
36F COLUMN - Pu DECONTAMINATION
36FW FISSION PRODUCT WASTE TO WASTE TREATMENT
36F5 HEXONE FROM ORGANIC STORAGE
36FP - 37BF Pu IN HEXONE
36F W WATER
37B COLUMN - Pu STRIPPING
37BP - 37DF Pu IN AQUEOUS
37D COLUMN - Pu DECONTAMINATION
37DW FISSION PRODUCT WASTE TO WASTE TREATMENT
37D5 HEXONE TO ORGANIC STORAGE
37DP - 37EF Pu IN HEXONE
37E COLUMN - Pu CONCENTRATION
37EP - 37FF Pu IN AQUEOUS
37E5 HEXONE TO ORGANIC TREATMENT
37E W WATER
37E5 HEXONE TO ORGANIC TREATMENT
37F COLUMN - Pu DECONTAMINATION
37FW FISSION PRODUCT WASTE TO WASTE TREATMENT
37F5 HEXONE FROM ORGANIC STORAGE
37FP - 38BF Pu IN HEXONE
37F W WATER
38B COLUMN - Pu STRIPPING
38BP - 38DF Pu IN AQUEOUS
38D COLUMN - Pu DECONTAMINATION
38DW FISSION PRODUCT WASTE TO WASTE TREATMENT
38D5 HEXONE TO ORGANIC STORAGE
38DP - 38EF Pu IN HEXONE
38E COLUMN - Pu CONCENTRATION
38EP - 38FF Pu IN AQUEOUS
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38F COLUMN - Pu DECONTAMINATION
38FW FISSION PRODUCT WASTE TO WASTE TREATMENT
38F5 HEXONE FROM ORGANIC STORAGE
38FP - 39BF Pu IN HEXONE
38F W WATER
39B COLUMN - Pu STRIPPING
39BP - 39DF Pu IN AQUEOUS
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39F COLUMN - Pu DECONTAMINATION
39FW FISSION PRODUCT WASTE TO WASTE TREATMENT
39F5 HEXONE FROM ORGANIC STORAGE
39FP - 40BF Pu IN HEXONE
39F W WATER
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40E W WATER
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40F COLUMN - Pu DECONTAMINATION
40FW FISSION PRODUCT WASTE TO WASTE TREATMENT
40F5 HEXONE FROM ORGANIC STORAGE
40FP - 41BF Pu IN HEXONE
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41EP - 41FF Pu IN AQUEOUS
41E5 HEXONE TO ORGANIC TREATMENT
41E W WATER
41E5 HEXONE TO ORGANIC TREATMENT
41F COLUMN - Pu DECONTAMINATION
41FW FISSION PRODUCT WASTE TO WASTE TREATMENT
41F5 HEXONE FROM ORGANIC STORAGE
41FP - 42BF Pu IN HEXONE
41F W WATER
42B COLUMN - Pu STRIPPING
42BP - 42DF Pu IN AQUEOUS
42D COLUMN - Pu DECONTAMINATION
42DW FISSION PRODUCT WASTE TO WASTE TREATMENT
42D5 HEXONE TO ORGANIC STORAGE
42DP - 42EF Pu IN HEXONE
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42EP - 42FF Pu IN AQUEOUS
42E5 HEXONE TO ORGANIC TREATMENT
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42FW FISSION PRODUCT WASTE TO WASTE TREATMENT
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42FP - 43BF Pu IN HEXONE
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43BP - 43DF Pu IN AQUEOUS
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43EP - 43FF Pu IN AQUEOUS
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43F COLUMN - Pu DECONTAMINATION
43FW FISSION PRODUCT WASTE TO WASTE TREATMENT
43F5 HEXONE FROM ORGANIC STORAGE
43FP - 44BF Pu IN HEXONE
43F W WATER
44B COLUMN - Pu STRIPPING
44BP - 44DF Pu IN AQUEOUS
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44DW FISSION PRODUCT WASTE TO WASTE TREATMENT
44D5 HEXONE TO ORGANIC STORAGE
44DP - 44EF Pu IN HEXONE
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44EP - 44FF Pu IN AQUEOUS
44E5 HEXONE TO ORGANIC TREATMENT
44E W WATER
44E5 HEXONE TO ORGANIC TREATMENT
44F COLUMN - Pu DECONTAMINATION
44FW FISSION PRODUCT WASTE TO WASTE TREATMENT
44F5 HEXONE FROM ORGANIC STORAGE
44FP - 45BF Pu IN HEXONE
44F W WATER
45B COLUMN - Pu STRIPPING
45BP - 45DF Pu IN AQUEOUS
45D COLUMN - Pu DECONTAMINATION
45DW FISSION PRODUCT WASTE TO WASTE TREATMENT
45D5 HEXONE TO ORGANIC STORAGE
45DP - 45EF Pu IN HEXONE
45E COLUMN - Pu CONCENTRATION
45EP - 45FF Pu IN AQUEOUS
45E5 HEXONE TO ORGANIC TREATMENT
45E W WATER
45E5 HEXONE TO ORGANIC TREATMENT
45F COLUMN - Pu DECONTAMINATION
45FW FISSION PRODUCT WASTE TO WASTE TREATMENT
45F5 HEXONE FROM ORGANIC STORAGE
45FP - 46BF Pu IN HEXONE
45F W WATER
46B COLUMN - Pu STRIPPING
46BP - 46DF Pu IN AQUEOUS
46D COLUMN - Pu DECONTAMINATION
46DW FISSION PRODUCT WASTE TO WASTE TREATMENT
46D5 HEXONE TO ORGANIC STORAGE
46DP - 46EF Pu IN HEXONE
46E COLUMN - Pu CONCENTRATION
46EP - 46FF Pu IN AQUEOUS
46E5 HEXONE TO ORGANIC TREATMENT
46E W WATER
46E5 HEXONE TO ORGANIC TREATMENT
46F COLUMN - Pu DECONTAMINATION
46FW FISSION PRODUCT WASTE TO WASTE TREATMENT
46F5 HEXONE FROM ORGANIC STORAGE
46FP - 47BF Pu IN HEXONE
46F W WATER
47B COLUMN - Pu STRIPPING
47BP - 47DF Pu IN AQUEOUS
47D COLUMN - Pu DECONTAMINATION
47DW FISSION PRODUCT WASTE TO WASTE TREATMENT
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47EP - 47FF Pu IN AQUEOUS
47E5 HEXONE TO ORGANIC TREATMENT
47E W WATER
47E5 HEXONE TO ORGANIC TREATMENT
47F COLUMN - Pu DECONTAMINATION
47FW FISSION PRODUCT WASTE TO WASTE TREATMENT
47F5 HEXONE FROM ORGANIC STORAGE
47FP - 48BF Pu IN HEXONE
47F W WATER
48B COLUMN - Pu STRIPPING
48BP - 48DF Pu IN AQUEOUS
48D COLUMN - Pu DECONTAMINATION
48DW FISSION PRODUCT WASTE TO WASTE TREATMENT
48D5 HEXONE TO ORGANIC STORAGE
48DP - 48EF Pu IN HEXONE
48E COLUMN - Pu CONCENTRATION
48EP - 48FF Pu IN AQUEOUS
48E5 HEXONE TO ORGANIC TREATMENT
48E W WATER
48E5 HEXONE TO ORGANIC TREATMENT
48F COLUMN - Pu DECONTAMINATION
48FW FIS

HW-18700

37

2M ≅ 476 g/L ≅ [redacted] ≅ 3.8 lbs/Gal

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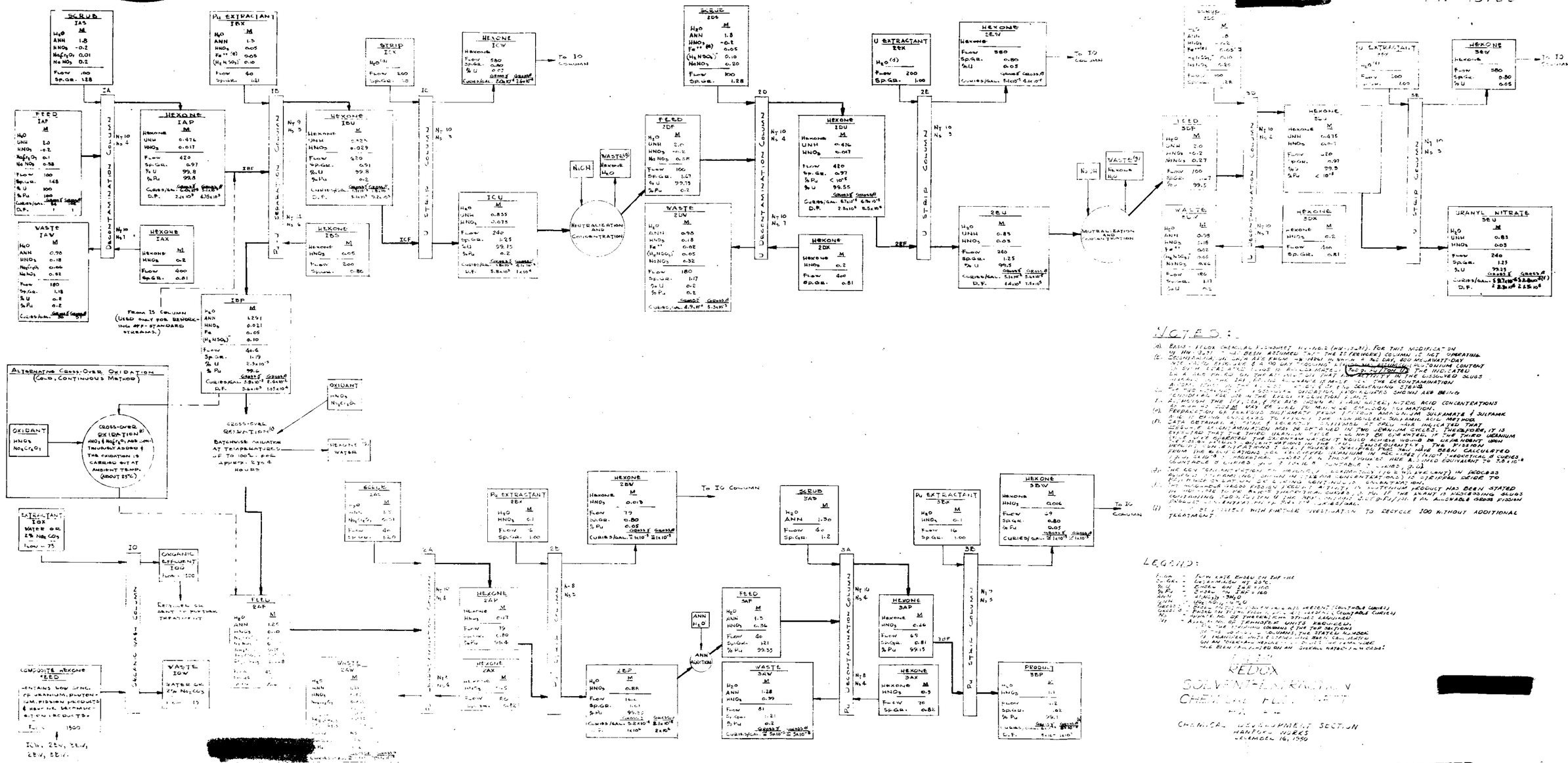

NOTES:

(a) BASIS - REDOX CHEMICAL FLOWSHEET HW-19612 (NOV. 31). FOR THIS MODIFICATION OF HW-19612 THE 1D COLUMN HAS BEEN ASSUMED AS THE IDENTICAL TO THE 1A (EXTRACTION) COLUMN IE NOT OPERATING UNDER SATURATION CONDITIONS. THE 1B COLUMN IS ASSUMED TO BE A 50 SIEVE TRAY SCRUB COLUMN WITH A 2:1 ORGANIC TO AQUEOUS FLOW RATIO. THE 1C COLUMN IS ASSUMED TO BE A 50 SIEVE TRAY STRIPPING COLUMN WITH A 1:2 ORGANIC TO AQUEOUS FLOW RATIO. THE 2D, 2E, 3D, AND 3E COLUMNS ARE ASSUMED TO BE IDENTICAL TO THE 1A, 1B, 1C, AND 1D COLUMNS RESPECTIVELY. THE NUMBER OF THEORETICAL STAGES SHOWN ARE BEING INVESTIGATED.

(b) IN 1A, THE 1DX, 2DX & 3DX FEED RATE SHOWN IS A CHAIN WATER, NITRIC ACID CONCENTRATIONS AS SHOWN ARE THE WAY TO BE EMPLOYED IN MAINTAINING.

(c) PERCENTAGE OF TECHNETIUM WHICH PASSES THROUGH THE FLOWSHEET AS SHOWN IS BEING INVESTIGATED. IT IS EXPECTED THAT THE MAJORITY OF THE TECHNETIUM WILL BE REMOVED IN THE 1A COLUMN BY REACTION WITH FERROUS AMMONIUM SULFAMATE & SULFAMIC ACID METHOD.

(d) DATA OBTAINED AT HANFORD LABORATORIES INDICATED THAT APPROXIMATELY 90% OF THE RUTHENIUM CONTAMINATION WAS REMOVED IN TWO URANIUM CYCLES. THEREFORE, IT IS EXPECTED THAT THE ADDITION OF A THIRD URANIUM CYCLE WILL BE BENEFICIAL IN THE DECONTAMINATION OF RUTHENIUM. THE DECONTAMINATION FACTOR WOULD ACHIEVE WOULD BE DEPENDENT UPON THE PRESENCE OR ABSENCE OF RUTHENIUM IN THE FEED SOLUTION. THE FISSION PRODUCT CONTAMINATION FACTORS GIVEN IN THE FLOWSHEET ARE CONSERVATIVE ESTIMATES BASED ON EXPERIENCE WITH THE REDOX OPERATIONS AT HANFORD. STATISTICAL FACTORS HAVE NOT BEEN CALCULATED FROM THE PLANT OPERATIONS DATA. THE FISSION PRODUCT CONTAMINATION IN THE FINAL URANIUM PRODUCT IS EXPECTED TO BE LESS THAN 1 CURIE PER TON OF URANIUM. THEORETICAL CURIES PER TON OF URANIUM IN THE FINAL PRODUCT ARE 2.1 CURIES PER TON FOR A 100 DAY COOLING PERIOD AND 0.8 CURIES PER TON FOR A 200 DAY COOLING PERIOD. THESE FIGURES ARE BASED ON 1 MW DAYS/TON OF URANIUM AND 0.1% FISSION. THE CURIE CONTENT OF THE FINAL PRODUCT IS EXPECTED TO BE LESS THAN THE THEORETICAL VALUES.

(e) THE DECONTAMINATION OF NEPTUNIUM (ASSUMED TO BE IN THE +6 VALENCY) IN PROCESS WASTES IS EXPECTED TO BE SIMILAR TO THAT OF PLUTONIUM. THE NEPTUNIUM CONCENTRATION IN THE FINAL PRODUCT IS ESTIMATED TO BE 0.1 GRAMS PER TON OF URANIUM. THE NEPTUNIUM CONCENTRATION IN THE FINAL PRODUCT HAS BEEN STATED ON THE BASIS OF THE THEORETICAL CHARGE, IE NO. 17 THE PLANT IS PROCESSING SLUGS CONTAINING 1000 GRAMS OF U235 PER TON OF URANIUM AND 0.1% FISSION PRODUCTS, THE NEPTUNIUM CONCENTRATION IN THE FINAL PRODUCT WILL BE 0.1 GRAMS PER TON.

(f) THE 1BV SOLUTION CONTAINS ONLY A SMALL AMOUNT OF URANIUM AND FISSION PRODUCTS. IT IS PLANNED TO RECYCLE THIS SOLUTION TO THE DISSOLVER FOR ADDITION TO THE NEXT BATCH OF SLUGS DISSOLVED. THE 1BV SOLUTION CONTAINS ONLY A SMALL AMOUNT OF URANIUM AND FISSION PRODUCTS. IT IS PLANNED TO RECYCLE THIS SOLUTION TO THE DISSOLVER FOR ADDITION TO THE NEXT BATCH OF SLUGS DISSOLVED. THE 1BV SOLUTION CONTAINS ONLY A SMALL AMOUNT OF URANIUM AND FISSION PRODUCTS. IT IS PLANNED TO RECYCLE THIS SOLUTION TO THE DISSOLVER FOR ADDITION TO THE NEXT BATCH OF SLUGS DISSOLVED.

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LEGEND:

FLOW - FLOW RATE BASED ON THE HR
SP. GR. - SPECIFIC GRAVITY AT 25°C
% U - BASED ON 238 U
% Pu - BASED ON 239 + 240
ANN - 1.0 M $Al(NO_3)_3$ - $9H_2O$
UNH - 1.0 M $UO_2(NO_3)_2$ - $6H_2O$
GRAMS/L - GRAMS OF URANYL NITRATE PRESENT (CONTROLLED CURIES)
CURIES/GAL - CURIES PER GALLON AT SPECIFIED GRAMS/L (CONTROLLED CURIES)
D.F. - DECONTAMINATION FACTOR REQUIRED
N_T - ACTUAL NO. OF TRANSFER UNITS REQUIRED.
N_S - THE NO. OF THEORETICAL STAGES AS SHOWN IN THE 1A, 1B, 1C, 1D, 2D, 2E, 3D, AND 3E COLUMNS, THE STAGES NUMBER 1 AT THE TOP OF THE COLUMNS & THE TOP SOLUTIONS LEAVE THE COLUMNS FROM THE TOP SOLUTIONS.
N_T & N_S - THE NO. OF TRANSFER UNITS & THEORETICAL STAGES FOR THE 1A, 1B, 1C, 1D, 2D, 2E, 3D, AND 3E COLUMNS ARE BASED ON AN EFFICIENCY OF 70% AS RECOMMENDED BY THE CHEMICAL ENGINEERING HANDBOOK. THE NUMBER OF STAGES HAVE BEEN CALCULATED ON AN OVERALL BASIS ONLY.

REDOX
SOLVENT EXTRACTION
CHEMICAL FLOWSHEET

CHEMICAL DEVELOPMENT SECTION
HANFORD WORKS
SEPTEMBER 16, 1950

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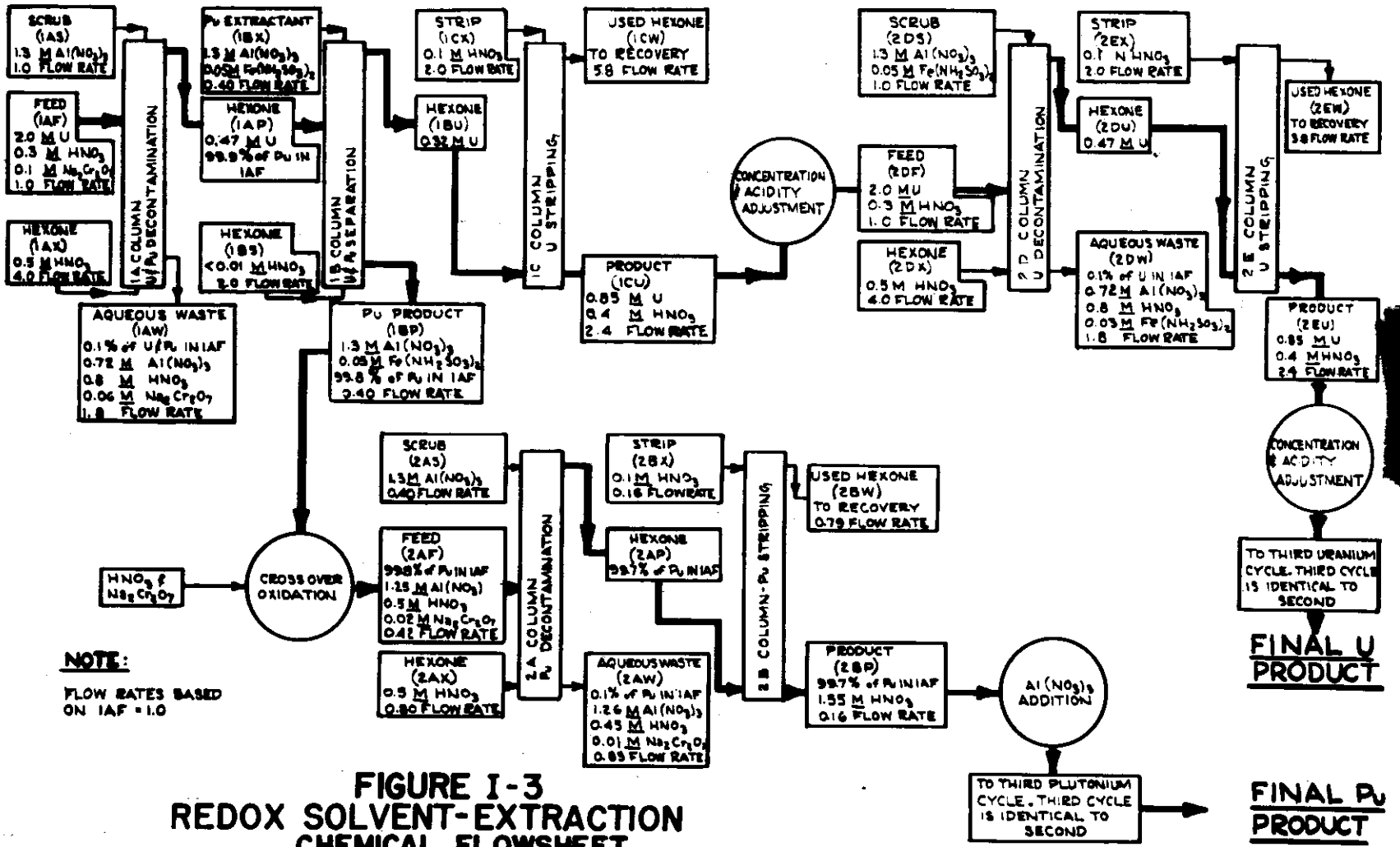

FIGURE I-3
REDOX SOLVENT-EXTRACTION
CHEMICAL FLOWSHEET
A.N.L. JUNE, 1948

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FIG. I-3

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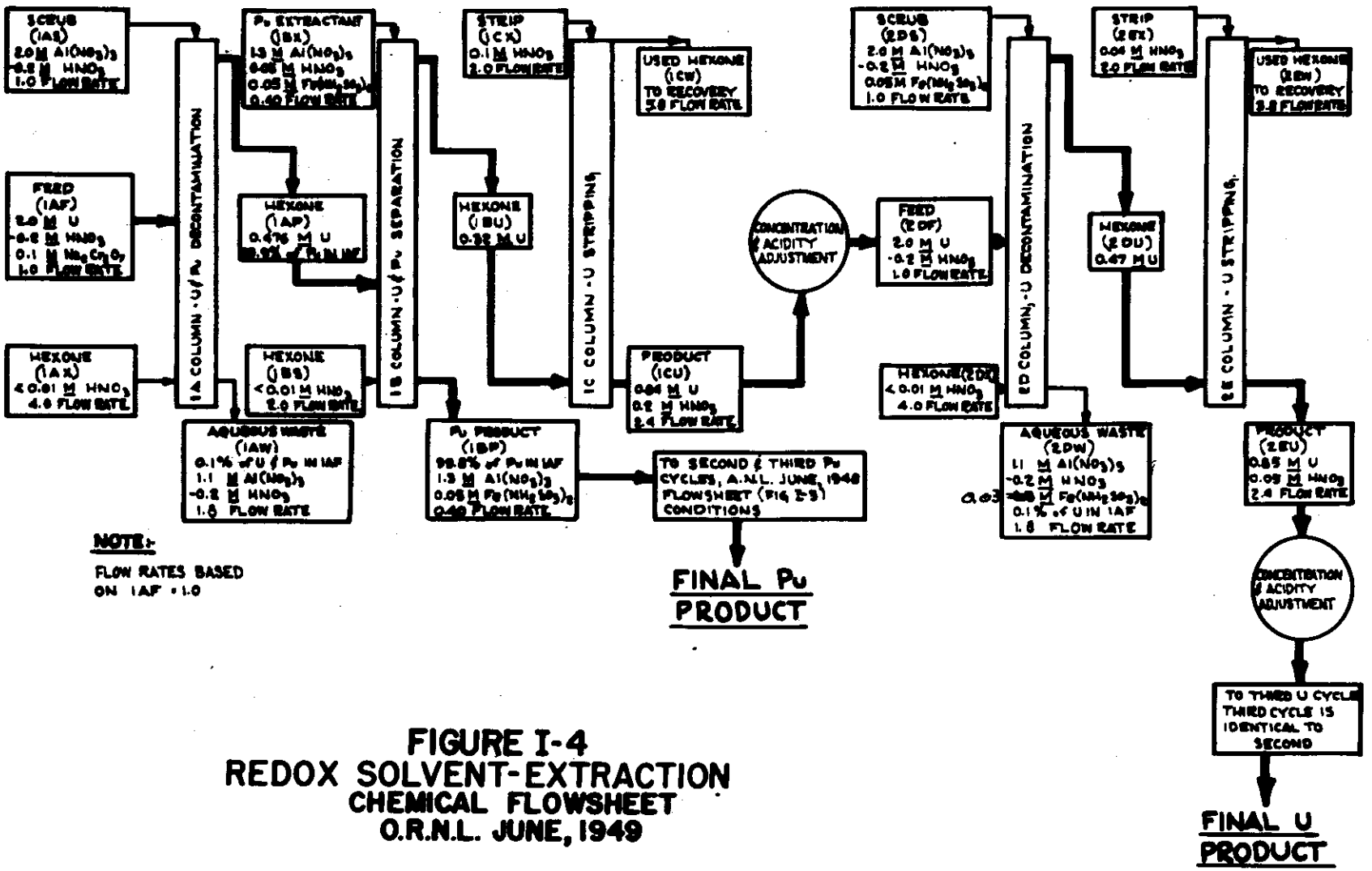

FIGURE I-4
REDOX SOLVENT-EXTRACTION CHEMICAL FLOWSHEET
O.R.N.L. JUNE, 1949

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FIG. I-4

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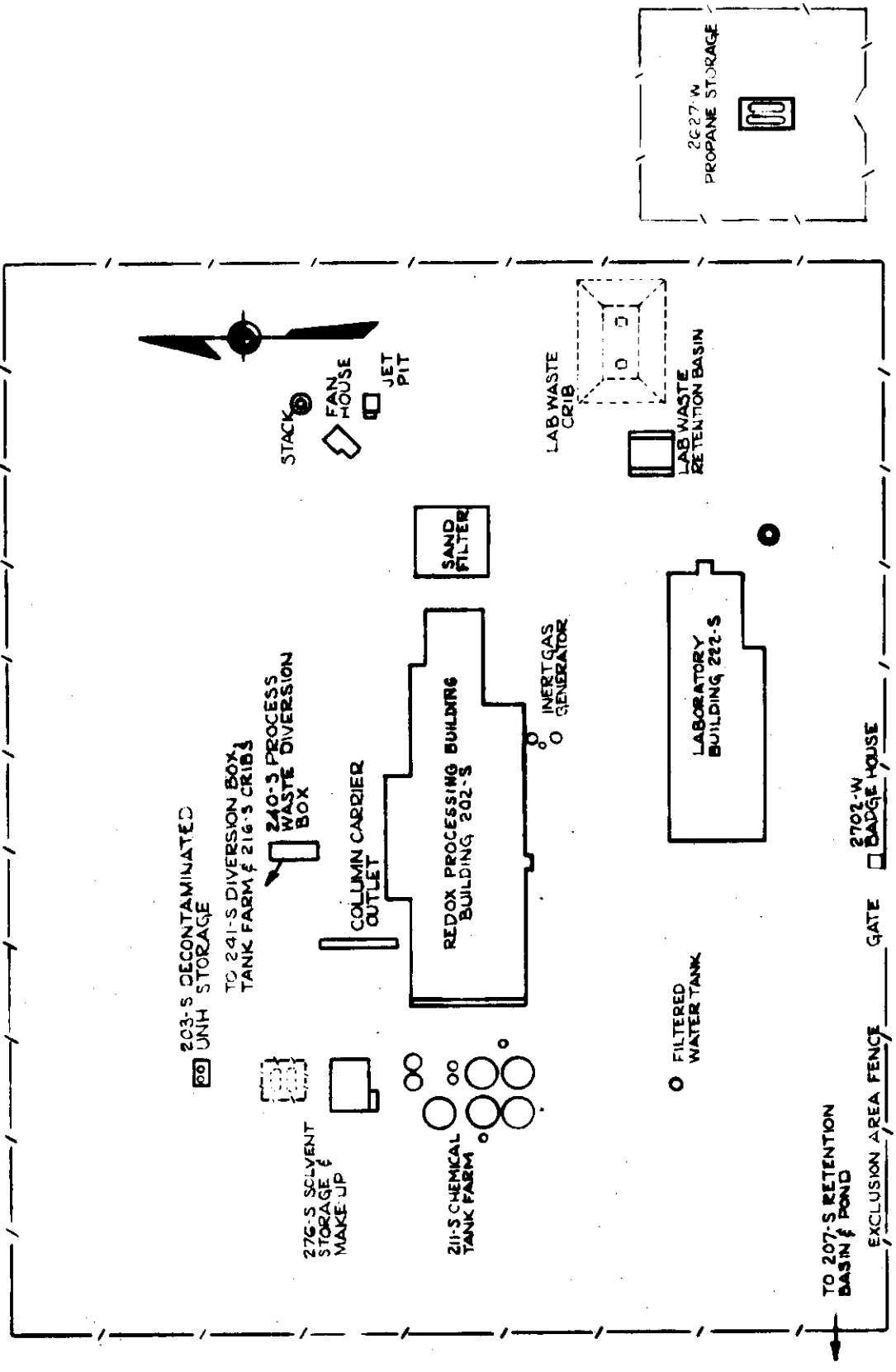
FIGURE I-5
SIMPLIFIED REDOX AREA LAYOUT



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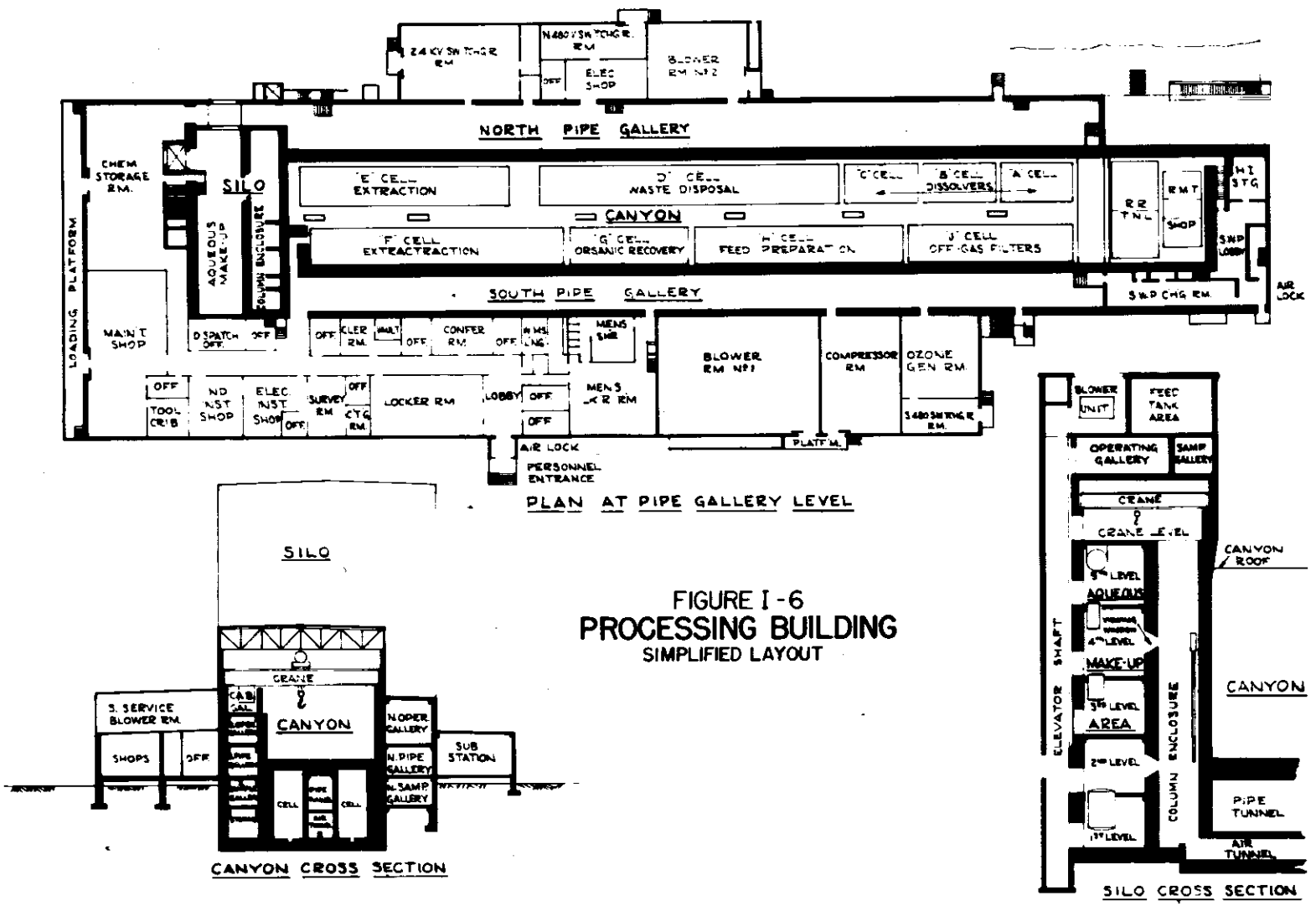

FIGURE I-6
PROCESSING BUILDING
SIMPLIFIED LAYOUT

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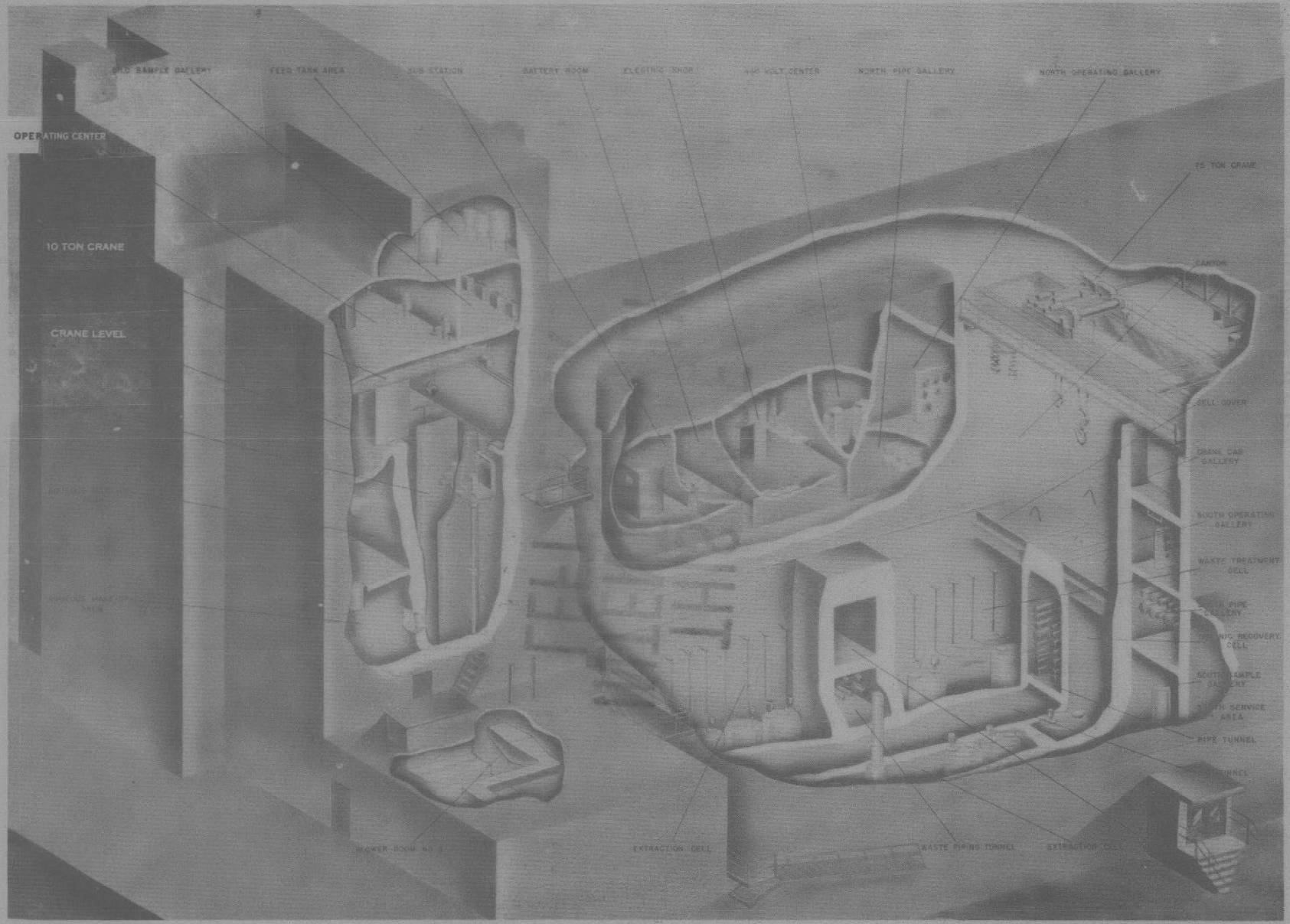

Figure I-7
REDOX PROCESSING BUILDING PERSPECTIVE CUTAWAY (FROM KLX 15-TR-138)

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TABLE I-8

ESTIMATED CHEMICAL AND UTILITY REQUIREMENTS
FOR THE REDOX PRODUCTION PLANT

Bases: Three Plutonium and Uranium Cycles
Uranium Processing Rate = 3.125 Short Tons/Day
Plutonium Enrichment Level = 400 Grams Pu/Short Ton U
HW No. 4 Flowsheet

Item	Requirements for 24 Hours Continuous Operation(a)(b)
100-lb./sq.in.ga. Steam	663,000 lb.
Raw Water	2,860,000 gal.
Demineralized Water	16,600 gal.
Hexone(c)	150 gal.
Caustic Soda (as 50% NaOH)	3,767 gal.
Nitric Acid (as 60% HNO_3)	1,852 gal.
Aluminum Nitrate (as 72% $Al(NO_3)_3 \cdot 9H_2O$)	4,370 gal.
Iron Powder	110 lb.
Soda Ash (as Na_2CO_3)	206 lb.
Sodium Dichromate (as $Na_2Cr_2O_7 \cdot 2H_2O$)	490 lb.
Sodium Nitrate (as $NaNO_3$)	1,045 lb.
Sulfamic Acid (as NH_2SO_3H)	394 lb.
Sulfuric Acid (as 66° Baumé)	50 lb.
Propane	165 gal.

(a) Process requirements only. Does not include service requirements.

(b) Does not include chemicals required for head-end Ru and Zr-Nb removal steps and for retreating hexone, if any.

(c) Estimated daily requirement if solvent retreatment is unnecessary.

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ESTIMATED IN-PROCESS INVENTORY OF PLUTONIUM AND URANIUM FOR THE REDOX PRODUCTION PLANT

Bases: Three Plutonium and three Uranium Cycles
Uranium Processing Rate = 3.125 Short Tons/Day
Plutonium Enrichment Level = 400 Grams Pu/Short Ton U

Process Section	Pounds of Uranium	Grams of Plutonium
Feed Dissolving and Storage (up to Oxidizer)	54,600	10,900
Feed Treatment (Oxidizer through IAF Make-Up)	6,250	1,250
First Extraction Cycle (IAF Feed Tank through ICU Concentrator)	10,200	1,800
Second Uranium Cycle (2DF Feed Tank through 2EU Concentrator)	2,700	1
Third Uranium Cycle (3DF Feed Tank through 3EU Sampler)	9,000	0
Second Plutonium Cycle (IBP Receiver through 2BP line)	0.1	370
Third Plutonium Cycle (3AF Feed Tank through 3BP Sampler)	0	640
Plutonium Concentration (Pre-Concentrator through PR Can)	0	900
Aqueous Waste Handling	60	13
Total	82,800	15,900

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48

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PART II: PROCESS

CHAPTER II. IRRADIATED SLUGS AND FISSION-PRODUCT DECAY

CONTENTS

Page

A. DESCRIPTION OF SLUGS 202

1. Dimensions, Composition and Preparation 202

2. Fabrication of the Canned Slugs 202

B. GROSS "COOLING" CURVES 203

C. SPECIFIC FISSION-PRODUCT DECAY CURVES 205

D. DECAY OF NEPTUNIUM 206

E. SLUG HANDLING PROCEDURE 207

REFERENCES 208

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CHAPTER II. IRRADIATED SLUGS AND FISSION-PRODUCT DECAY

A. DESCRIPTION OF SLUGS

1. Dimensions, Composition and Preparation

Uranium slugs as received for processing in the Redox Plant are cylindrical in shape and enclosed in an aluminum jacket which is sealed to the uranium with an aluminum-silicon alloy bonding layer. A typical canned uranium slug is 4.375 in. long and 1.450 in. in diameter.

The older standard "8-in." canned uranium slugs (8.70 in. long and 1.440 in. in diameter) are no longer used because neutron bombardment of the uranium metal causes it to suffer dimensional changes. These changes (especially warping) made "pushing" of some of the 8-in. slugs from the pile very difficult with the result that a standard ("4-inch") canned slug is now made 4.375 in. in length. The shorter four-inch slugs warp also, but, for the same radius of curvature, deviate from a straight cylinder by a smaller distance than the longer slugs.

Detailed dimensions and compositions of the several constituent parts of a standard four-inch canned uranium slug are given in Figure II-1. Macro components of a standard four-inch slug are as follows:

Component	Element		Weight
Core	Uranium		3.93 lb.
Bonding layer, total	(2S aluminum*	8.84 g.)	10 grams
	(Silicon	1.15 g.)	
	(Tin	0.01 g.)	
Aluminum jacket, cap plus can	2S aluminum*		50 grams
Can only	2S aluminum*	42 g.	
Cap only	2S aluminum*	8 g.	

* The minimum Al content of 2S aluminum is 99.0%. A typical composition is 99.2% Al, 0.5% Fe, 0.25% Cu, and traces of Si, Mg, Mn, and Ti.

2. Fabrication of the Canned Slugs

In order to show how the molten-metal baths used in canning influence the composition of the bonding layer, a simplified flow sketch of the process for canning the machined uranium slugs is presented below.

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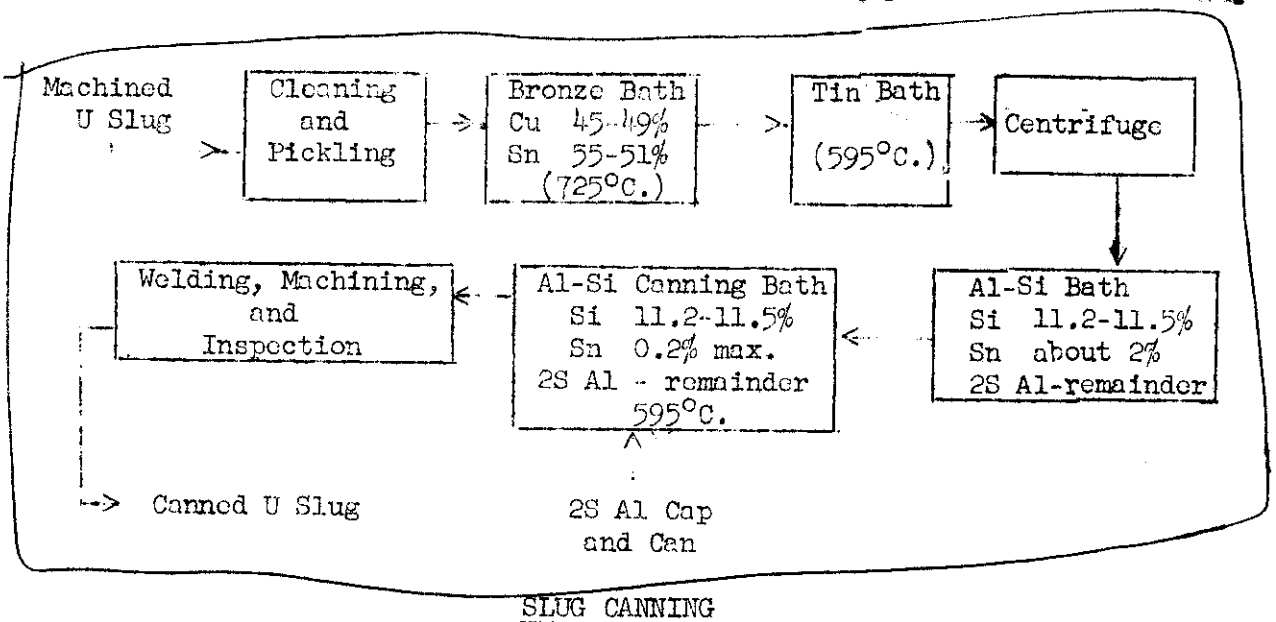

SLUG CANNING

Thus the Al-Si bonding layer has the composition of the Al-Si bath (i.e. 11.2 to 11.5% Si, approximately 88.5% 2S aluminum), with the low concentration of tin (0.2% max.) originating from the tin bath. The "compound layer", chiefly tin with a thickness of less than one mil, results directly from the tin bath.

B. GROSS "COOLING" CURVES

The canned uranium slugs are exposed in the piles for periods ranging from about 9-1/2 months (central zone) to about 2 years (fringe zone). A four-inch slug taken directly from the pile contains on the order of 2,000 curies of total activity due to the presence of radioactive isotopes resulting from the fission of U^{235}. Accordingly, slugs are "cooled" for a period of from 40 to 90 days to allow the short-lived isotopes to decay to negligible radioactivity levels.

Approximately one hundred short-lived radioactive isotopes (half-life 1 day or less) are present in significant amounts in irradiated uranium during "cooling". About 20 of these are directly produced by fission of U^{235} (and Pu^{239}) in yields above 1%. A few examples of the more abundant short-lived fission products are as follows:

Radioactive Isotope (a)	Half Life	Fission Yield %(b)
Sr^{91}	9.7 hr.	5.6
Zr^{97}	17.0 hr.	6.1
Ru^{105}	4.4 hr.	1.0
I^{131}	8.0 days	3.0
Xe^{133}	5.3 days	4.7

Notes:

(a) All of the isotopes listed are longer half-lived daughters of parent beta emitters.

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(b) The probability that a nuclide of any given mass number will occur during fission is called its fission yield. Since the elemental composition of the fission products changes with time because of beta decay, the fission yield is based on the mass number rather than the atomic number of the fission product. Thus the 5.6% fission yield for Sr^{91} indicates that for each 100 atoms of U^{235} which fission in the pile, 5.6 atoms of mass number 91 are produced.

The overall change in radioactivity with "cooling" time for uranium which has been irradiated in a pile for various lengths of time and then removed is shown in Figure II-2. The curves are useful in determining the quantity of radioactivity in uranium to be processed in the Redox Plant. Figure II-2 is independent of the quantity of uranium present in the pile. For example, either a one-ton or a ten-ton uranium pile operating at one-watt total power for the same length of time will produce the same amount of fission products per pile. (However, the ten-ton pile will produce only a tenth of the amount of fission products per ton.)

The following calculation of the total curies per short ton of uranium irradiated for 100 days at 400 megawatts in a 200-short-ton pile and "cooled" for 50 days illustrates the application of Figure II-2. From the figure, the total number of curies/pile for slugs irradiated for 100 days (parameter) at 1 watt and "cooled" 50 days (abscissa) is 0.128 (read on the ordinate). Thence, the number of curies/short ton of uranium in a 200-short-ton pile operated at a power level of 400 megawatts (i.e. 400×10^6 watts) is:

$$\frac{0.128}{200} \times (400 \times 10^6) = 2.6 \times 10^5.$$

Figure II-2 shows that the amount of radioactivity decreases quite rapidly with increase in "cooling"time. The following table provides a quantitative illustration of the rapidity of "cooling":

"Cooling" Time	Curies/Short Ton of U	Watts/Short Ton of U
30 minutes	---	about 3×10^4
16 days	4.8×10^5	2.4×10^3
30 days	3.6×10^5	1.8×10^3
50 days	2.6×10^5	1.2×10^3
100 days	1.4×10^5	6.1×10^2
200 days	6.1×10^4	2.6×10^2

Some direct experimental measurements of gamma radioactivity are reported in Document HW-17781[7]. The radioactivity of uranium slugs exposed for 160 and 370 days, respectively, was measured with a type G.L. 563 ionization chamber. The results after conversion to a unit power level of one megawatt per short ton of uranium resulted in the curves plotted on Figure II-3. The curves for the 370-day irradiated uranium gradually rise above those for the 160-day irradiated uranium. This trend is in agreement with theoretically expected results, since

the concentration of the short-lived gamma-emitting isotopes will reach saturation after a relatively short irradiation, while that of the long-lived components will continue to increase as the exposure continues.

C. SPECIFIC FISSION-PRODUCT DECAY CURVES

Decay curves for a number of radioactive isotopes important to the Redox process (see Chapter IV) have been calculated and are shown in Figure II-4. The quantity of fission products originally present was based on a uranium exposure of 400 megawatt-days/ton over a period of 360 days. Theoretical of "absolute" curies as well as "countable" curies are shown for the total beta and gamma radiation. The activities of specific isotopes are presented in terms of "countable" curies.

A (theoretical or absolute) curie is defined as the radioactivity of a source of radiation which decays at such a rate that 3.7×10^{10} atoms change per second. It is almost exactly the radioactivity of the amount of radon in equilibrium with 1 gram of radium. Because of the limitations of ordinary radiation counters, absolute curies are difficult to determine. The "countable" curies, in terms of which most of the data in Figure II-4 are expressed, have the practical advantage of being subject to comparatively easy and reproducible determination. Determination of the number of "countable" curies, in the sense in which the term is used here, involves the "counting" of the sample under specified conditions with standard counting instruments, such as the B.G.O. counter in use at Hanford Works. The counting conditions are specified in detail in Document HW-17091(5). The counting efficiency of the standard counters, and hence the ratio of absolute to "countable" curies, is a function of the particle (or quantum) energy of the radiation measured. Although it is not possible to assign exact values to this ratio, the following are approximate values for beta particles and gamma rays of some typical energies:

Particle or Quantum Energy, M.e.v.	Ratio of Absolute to "Countable" Curies	
	Beta	Gamma
0.1	∞ (not counted)	10
0.15	50	8
0.6	4	3
2.0	2	1.2

The conversion of "countable" to absolute curies is further discussed in Document HW-17091(5).

On a basis of 400 megawatt-days/ton exposure with 90 days "cooling", the Redox IAF (feed) solution is expected to contain the following amount of radioactive fission products.

	Absolute Curies/Gal.(a)	Countable Curies/Gal.(a)
Total beta radioactivity	330	100
Total gamma radioactivity	230	55

(a) Based on the assumption that no radioactivity is removed in head-end treatment.

The total radioactivity as contributed by individual isotopes with an irradiation and "cooling" history as above is presented in Table II-5. The fission products (Ru, Zr, Nb, and Ce) listed at the top of Table II-5, under "A", are of primary importance because they control the decontamination factor obtainable in the Redox process. The fission products listed in the table under "B" also contribute largely to the radioactivity of the IAF. However, because of their low extractability, they are almost completely removed in the IAW (waste) stream.

As noted in Section B, above, about twenty radioisotopes are directly produced during fission of U^{235} in fission yields above 1% which, however, have such short half-lives (1 day or less), that they are negligible as compared to the longer lived isotopes in considering a IAF feed solution(4)(6). Two comparatively short-lived radioactive isotopes of importance are I^{131} (8-day half-life) and Xe^{133} (5.3-day half-life) because they are emitted as gases during dissolver operation.

D. DECAY OF NEPTUNIUM

Plutonium is formed during irradiation in the piles according to the following reaction:

$$U^{238}_{92} + N^{1}_{0} \longrightarrow U^{239}_{92} \xrightarrow{\beta^-} N^{239}_{93} \xrightarrow{\beta^- + \text{a soft gamma ray}} Pu^{239}_{94}$$

Before the "cooling" period, the Np^{239}, with a half-life of 2.3 days, is present in the irradiated slugs in significant amounts, for example, 3% of the weight of plutonium at shutdown after 100 days of pile operation. Because of its short half-life, decay of Np^{239} after discharge of the slugs from the pile, is rapid and follows the equation:

$$\frac{N}{N_o} = e^{-0.301t},$$

Where N = amount of Np^{239} present at time t;

N_o = amount of Np^{239} originally present;

t = "cooling" time, days.

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Thus, uranium slugs "cooled" for 60 days have only a millionth of a per cent of the original Np^{239} present at discharge.

$$\frac{N}{N_o} = e^{-(0.301)(60)} = e^{-18.06} = 1.5 \times 10^{-8}$$

$$\frac{100\ N}{N_o} = \frac{(100)\ (1.5 \times 10^{-8})}{1} = 1.5 \times 10^{-6}\%$$

E. SLUG HANDLING PROCEDURE

The uranium slugs are received in the 200 Areas in buckets containing about 1,100 pounds (approximately 280 four-inch slugs) of uranium. The slugs (still contained in the buckets) are stored in the 212 Building Storage Basin under 19 to 20 feet of water for a period of from 40 to 90 days. After the decay period, the bucket of slugs is placed in a lead cask mounted on a railroad flat-car. A drawing of the lead cask appears in Chapter XVI. The flat-car carrying two casks (therefore, two buckets, or a total of about 2,200 pounds of uranium) is then transferred to the Redox Processing Building (202-S). The uranium coming into the 202-S Building is charged directly from the cask car to the dissolvers by means of the overhead crane. Charging of the dissolver is completed by the crane operator, who lifts the cover off the car, unlocks the cask with an impack wrench, picks up the cask lid and places it on one end of the car. The bucket is then lifted from the cask, brought over the dissolver, and lowered into the charging opening. As the crane operator continues to lower the bucket yoke, the lower lugs of the bucket catch on hooks in the dissolver opening causing the bucket to tip forward and to dump the slugs into the dissolver. Drawings of the dissolver and of the centering lugs appear as Figures XIII-3 and XIII-4, respectively, in Chapter XIII.

After 7 buckets have been unloaded, the dissolver lid and cell cover are replaced. Then, the coating removal procedure as described in Chapter III may be started.

Because of the relatively high radiation levels existing on the canyon deck at such times, it is unsafe for personnel to remain on the canyon deck during the charging operation while buckets are in the air. No personnel are permitted in the canyon or railroad tunnel when a slug bucket is being transported. It may also be unsafe in the tunnel or canyon when a cask lid is removed.

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(4) HW-14261 Estimated Fission-Product Distribution in Redox Process Streams (H.W. No. 1 Flowsheet). D. P. Granquist. 8-26-49.

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(6) HW-17415 Activity of Fission Products. P. R. Gillette. 4-14-50.

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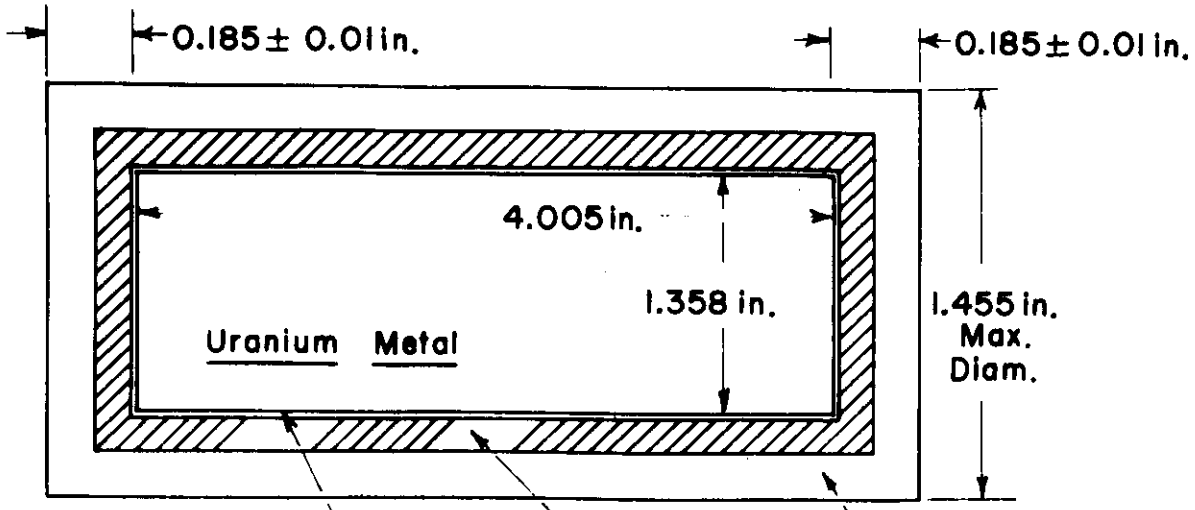
Figure II-1

STANDARD 4-INCH CANNED URANIUM SLUG



Layer	"Compound" Layer	Al-Si "Bonding" Layer	2S Aluminum Can
Thickness	< 1 mil	10-25 mils	25 mils
Composition	Chiefly Tin	Si 11+% Al 87+%	Al 99+%

Impurities in the uranium metal, from typical analyses:

Element	Concentration Parts Per Million
Carbon	450
Nitrogen	60
Iron	50-100
Silicon	50
Cobalt, Zinc	< 100
Potassium	< 50
Copper, Aluminum	< 20
Other elements (individually)	< 10
Typical analysis for: Cd	< 1
B	< 0.2

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FIGURE II-2

IRRADIATED URANIUM "COOLING" CURVES

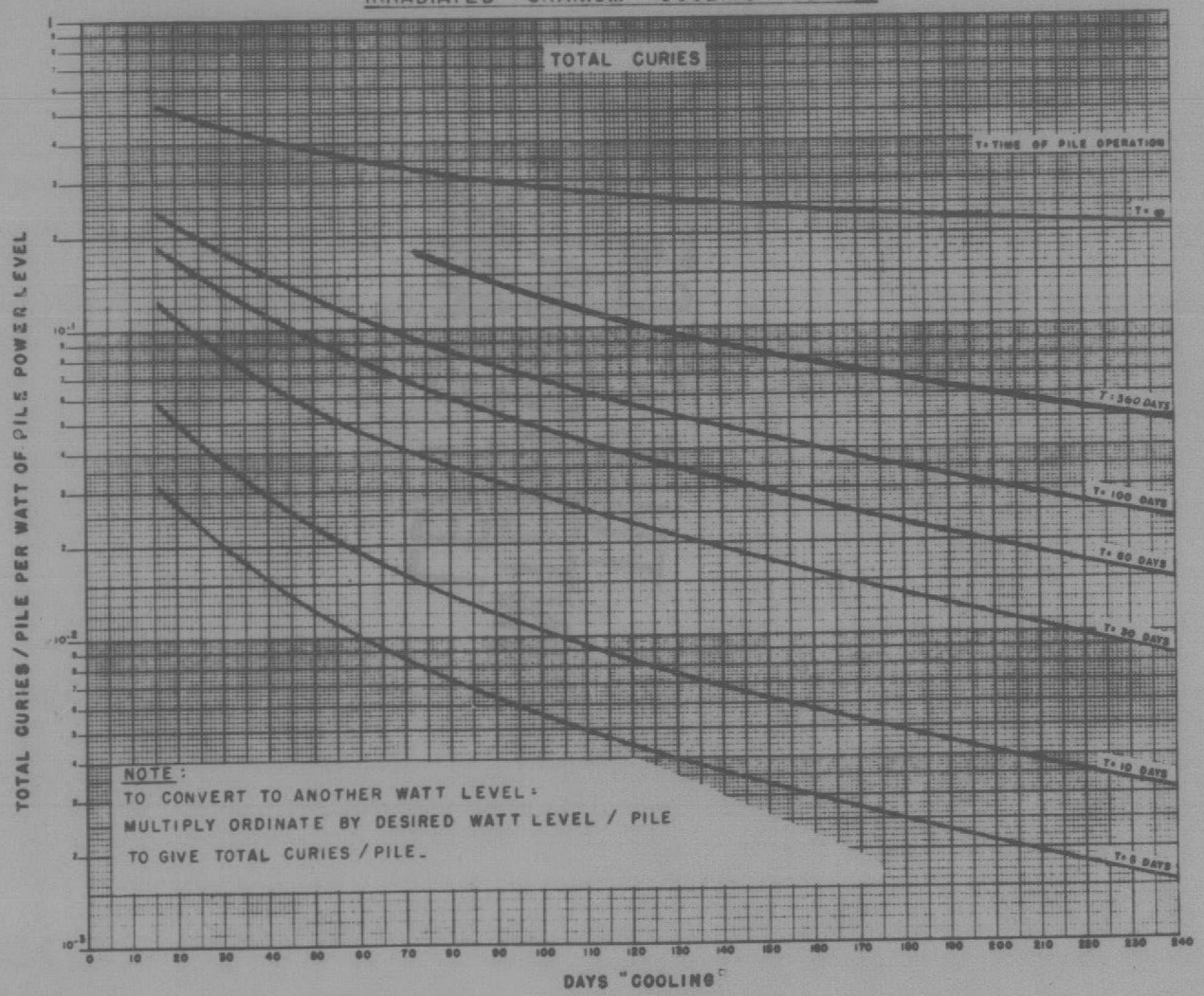

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FIGURE II-2

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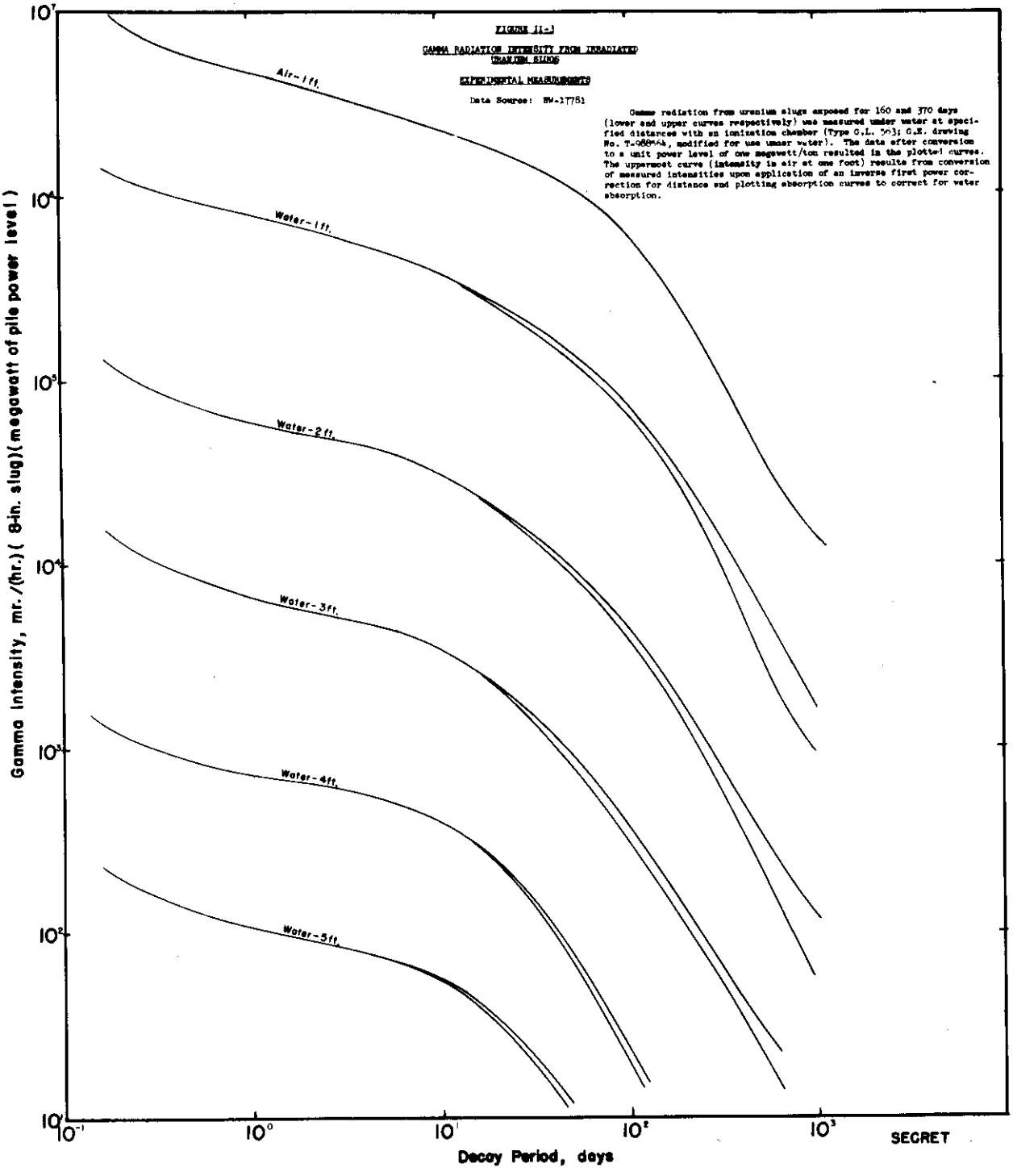
FIGURE II-1

GAMMA RADIATION INTENSITY FROM IRRADIATED URANIUM SLUGS

EXPERIMENTAL MEASUREMENTS

Data Source: HW-17751

Gamma radiation from uranium slugs exposed for 160 and 370 days (lower and upper curves respectively) was measured under water at specified distances with an ionization chamber (Type G.L. 503; G.E. drawing No. T-98868, modified for use under water). The data after conversion to a unit power level of one megawatt/ton resulted in the plotted curves. The uppermost curve (intensity in air at one foot) results from conversion of measured intensities upon application of an inverse first power correction for distance and plotting absorption curves to correct for water absorption.



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Elapsed Time From Pile Discharge, [redacted]

0.1 1.0 10 100

Countable Curies/10^6 Grams Uranium

0.1 1.0 10 100 1000 10000

Zr Beta
Zr Gamma
Ru Beta
Ru Gamma
Ce Beta
Cs Beta
Cs Gamma
Ce Gamma
Gross Absorber Beta Curies
Sr Beta
Gross Gamma
Gross Beta
Gross Absolute Gamma Curies

FIGURE II-4

SPECIFIC FISSION-PRODUCT DECAY CURVES

Source of Data: BW-17091
Basis: 400 Megawatt-Days/Ton Integrated Exposure Over 360 Days

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FISSION [redacted] PLANT OPERATION

A. Fission Products Important Because They Control Contamination Factors Obtained in the Redox Process

Fission Product	Fission Yield, %(d)	Half-Life	Radio-activity	Energy, M.e.v.	Absolute Curies/G. of U(c)	Absolute Curies/Mol. of U(c)
Ru^{103}	3.0	45 days	Beta	0.35	0.0044	7.9
				0.66	0.0044	7.9
			Gamma	0.51	0.0044	7.9
Ru^{106}-Rh^{106}(a)	0.5	290 days	Beta	2.30(b)	0.0004	0.8
				3.45(b)	0.0010	1.4
			Gamma	0.42(b)	0.0004	0.7
				0.73(b)	0.0004	0.7
				1.25(b)	0.00004	0.07
Zr^{95}-Nb^{95}(a)	6.2	65 days	Beta	0.39	0.023	41.4
				1.13	0.0008	0.9
			Gamma	0.21(b)	0.022	39.3
				0.73	0.021	37.6
				0.94	0.0016	1.0
Nb^{95}	6.2	38.7 days	Beta	0.15	0.018	60.0
			Gamma	0.76	0.018	60.0
Ce^{141}	6.1	28 days	Beta	0.44	0.0056	10.1
			Gamma	0.13	0.0056	10.1
Ce^{144}-Pr^{144}(a)	5.2	275 days	Beta	0.35	0.025	44.3
				1.80(b)	0.0025 (?)	4.4 (?)
				2.96(b)	0.022	39.8
			Gamma	0.20(b)	0.025	44.3
				1.96(b)	0.0025 (?)	4.4 (?)

B. Other Fission Products Important Because of Their Relative Abundance

Kr^{85}	0.33	9.7 years	Beta	0.7	0.00023	0.4
Sr^{89}	4.7	54 days	Beta	1.46	0.0152	27.4
Sr^{90}-Y^{90}(a)	5.2	25 years	Beta	0.61	0.00146	2.6
				2.18(b)	0.00146	2.6
Y^{91}	5.6	57 days	Beta	1.54	0.0210	38.5
Te^{129}-Te^{129}(a)	0.4	32 days	Beta	1.3(b)	0.00064	1.2
			Gamma	0.11	0.00064	1.2
				0.3(b)	0.00064	1.2
				0.8(b)	0.00064	1.2
Cs^{137}-Ba^{137}(a)	6.1	33 years	Beta	0.52	0.00117	2.1
				1.10	0.00006	0.1
			Gamma	0.69(b)	0.00117	2.1
Ba^{140}	6.2	12.8 days	Beta	0.47	0.00013	0.2
				1.00	0.00038	0.7
			Gamma	0.53	0.00013	0.2
La^{140}(a)	6.2	40 hours	Beta	0.91(b)	0.000002	0.2
				1.40(b)	0.000413	0.7
				2.18(b)	0.000060	0.1
			Gamma	0.49(b)	0.000060	0.1
				0.87(b)	0.000060	0.1
				1.65(b)	0.000045	0.8
				2.14(b)	0.000060	0.1
Pr^{143}	5.6	13.8 days	Beta	0.84	0.00062	1.1
Nd^{147}	3.0	11.8 days	Beta	0.77	0.000064	0.1
				0.96	0.000096	0.2
			Gamma	0.58	0.000064	0.1
Pm^{147}	3.0	3.7 years	Beta	0.22	0.00506	9.1

C. All Other Radioactive Fission Products

	Beta	ca. 0.005	ca. 10
	Gamma	ca. 0.003	ca. 5

Total

Beta		0.183	330
Gamma		0.128	230

(a) Quantity of emitted radioactivity is governed by decay of long-lived parent.
(b) Activity due to daughter element.
(c) The basis for the absolute curies reported above is 400 megawatt-days/ton exposure with 90 days "cooling." These numbers are based on the assumption that no radioactivity has been removed from the IAF by volatilization of Ru or by scavenging of Zr and Nb (i.e., by the "head-end" treatments). For a definition of absolute curies, see text.
(d) The probability that a nuclide of any given mass number will occur during fission is called its fission yield. Since the elemental composition of the fission products changes with time because of beta decay, the fission yield is based on the mass number rather than the atomic number of the fission product. Thus the 3.0% fission yield for Ru^{103} indicates that for each 100 atoms of U^{235} which fission in the pile, 3.0 atoms of mass number 103 are produced.

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PART II: PROCESSES, continued

CHAPTER III. FEED PREPARATION

CONTENTS

	Page
A. JACKET REMOVAL	303
1. General	303
2. Chemistry of Jacket Removal	303
3. Effect of Sodium Hydroxide Concentration	303
4. Effect of Sodium Nitrate Concentration	304
5. Slug Rinsing	304
B. DISSOLUTION	305
1. Properties of Uranium	305
2. Chemistry of Uranium Dissolving	305
3. Chemistry of Plutonium Dissolving	306
4. Distribution of Fission-Product Elements During Dissolution	306
5. General Discussion	307
C. OXIDATION AND RUTHENIUM DISTILLATION	309
1. Introduction	309
2. Plutonium Oxidation	309
2.1 Chemistry	309
2.2 Oxidation techniques	311
3. Ruthenium Distillation	311
3.1 General	311
3.2 Ruthenium distillation by means of ozone	312
3.3 Ruthenium distillation by means of potassium permanganate	314
D. CLARIFICATION AND SCAVENGING	315
1. Introduction	315
2. Clarification	317
3. Scavenging of Zirconium and Niobium	318
3.1 Scavenging with Super Filtrol F.O.	318
3.2 Scavenging with co-formed manganese dioxide	320
4. Centrifugation Without Scavenging	322

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DECLASSIFIED

CONTENTS

Page

E. IAF ADJUSTMENT 323

1. General 323
2. Acid Deficiency 323
3. Methods 323

F. GAS TREATMENT 324

1. General 324
2. Removal of Iodine with Silver Reactor 324
3. Scrubbing of Dissolver Off-Gas 326
4. Scrubbing of Ruthenium Tetroxide 327

G. PROCEDURE 328

1. Normal Procedure 328
   1.1 General 328
   1.2 Coating removal and dissolving 328
   1.3 Dissolver off-gas treatment 330
   1.4 Metal solution storage 331
   1.5 Oxidation and scavenging 331
      1.51 $KMnO_4$ procedure with MnO_2 scavenging 331
      1.52 $KMnO_4$ procedure without scavenging 332
      1.53 Ozone-Filtrol procedure 332
      1.54 Modified procedures 333
   1.6 Ruthenium scrubbing 333
   1.7 IAF adjustment 334
2. Remedy of Off-Standard Conditions 334
   2.1 Excessive fission-product activity in Stack 334
   2.2 Greater than normal Ru, Nb, or Zr activity in IAF 334
   2.3 Carry-over of fines from centrifugation 335
   2.4 Excessive U or Pu loss with filter cake 335
   2.5 Formation of plutonium (IV) polymer 335
   2.6 Necessity of rapidly arresting uranium dissolution reaction 335
   2.7 Sludge build-up in the Dissolver 335

REFERENCES 337

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CHAPTER III. FEED PREPARATION

A. JACKET REMOVAL

1. General

The first step in preparing the radioactive slugs discharged from the piles for uranium-plutonium-fission-product separation in the Extraction Battery is the removal from each slug of the aluminum jacket and the aluminum-silicon bonding layer between the jacket and slug proper. This operation together with the subsequent slug-dissolution step is performed in any of the three Dissolvers. A description of the Dissolvers is given in Chapter XIII. The jacketed slugs are described in Chapter II.

2. Chemistry of Jacket Removal

The aluminum slug jacket is removed by dissolution in a solution consisting of about 10% sodium hydroxide and 20% sodium nitrate at boiling temperature, about 100 to 108°C. The sodium nitrate suppresses the formation of hydrogen which would otherwise evolve in high concentrations according to the following reaction:

$$2Al+2NaOH+2H_2O \longrightarrow 2NaAlO_2+3H_2.$$

In the presence of sodium nitrate, either of the following reactions may take place:

$$8Al+5NaOH+3NaNO_3+2H_2O \longrightarrow 8NaAlO_2+3NH_3$$

$$2Al+2NaOH+3NaNO_3 \longrightarrow 2NaAlO_2+3NaNO_2+H_2O.$$

Data accumulated during plant-scale coating-removal operations have indicated that roughly half of the aluminum is dissolved according to each reaction. However, even with the use of sodium nitrate the formation of hydrogen is not eliminated entirely. Data have indicated the presence of up to 1% hydrogen in the off-gas with the 10% NaOH, 20% $NaNO_3$ procedures.(12)

3. Effect of Sodium Hydroxide Concentration

Laboratory experiments have shown that a NaOH/Al mole ratio of 1.25 provides an adequate sodium hydroxide excess for dissolution of the aluminum. However, this ratio is not great enough to insure that Al_2O_3 will not precipitate if the solution is allowed to stand for a day. Results have shown that a NaOH/Al mole ratio of 1.65 prevents precipitation even if the solution is held for long periods of time. In the Redox Plant this ratio is approximated by the use of about 1370 lb. of 50% NaOH to dissolve about 269 lb. of coating material from a 7700-lb. uranium charge.

Aluminum is vigorously attacked by sodium hydroxide over a tested concentration range of 5 to 50% NaOH. The reaction rate increases with

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increased caustic strength and with temperature. The penetration rate, which is a measure of the rate of attack, approximately triples from 60°C. to 100°C. (if concentrations are maintained constant at about 10% NaOH and 20% $NaNO_3$ over this temperature range) to an average value of about 4 to 6 mils/minute at 100°C.(12) Uranium loss by caustic attack is very slight in solutions up to 30% NaOH, but the rate of solution becomes appreciable in 50% NaOH. In the coating-removal step, dilute caustic (10% NaOH) is desirable to limit the rate of reaction and to obtain sufficient solution volume to cover the slugs in the Dissolver without using an unreasonably large excess.

Precipitation of Al_2O_3 may occur in the coating waste if the caustic concentration is too low. Bismuth Phosphate Plant practice has maintained a caustic concentration of about 5% in the coating-removal waste. No Al_2O_3 precipitates before the solution is sent to underground storage under these conditions. Redox Plant practice in this respect is identical, the 1370-lb. NaOH charge representing a caustic concentration of about 5% in the coating waste solution. The pH of the coating waste solution is about 12 to 13.

Sodium hydroxide dissolves the aluminum-silicon alloy, but the thin tin-aluminum-silicon-uranium compound layer on the surface of the slug is only partially removed by the undercutting and disintegrating action of the caustic. The coating waste solution contains less than 0.1% by weight of these suspended solids, and a portion of the suspended material is removed from the Dissolver with the coating waste.

4. Effect of Sodium Nitrate Concentration

The coating-removal step is comparatively insensitive to variations in sodium nitrate concentration. Concentrations as low as 10% are satisfactory for suppression of hydrogen formation, but there is some evidence that solid residues are more completely removed from the Dissolver with the coating waste solution if the coating-removal solution contains about 20% sodium nitrate.

5. Slug Rinsing

A water flush of the slugs after coating waste has been removed serves to flush the Dissolver of residual alkalinity and also to remove additional suspended solids.

A 5% nitric acid rinse is added to the Dissolver following the removal of the water flush. The dilute acid serves to remove, at least partially, the remaining thin aluminum-silicon-tin-uranium scale left on the surface of the slug after jacket removal. Recent developments have indicated the possibility of dispensing with this acid rinse if the small additional amount of aluminum, tin, and silicon in the uranium solution is not detrimental to subsequent process operations. (See Subsection D2, Clarification.)

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B. DISSOLUTION

1. Properties of Uranium

After the aluminum jacket is removed, the bare uranium slug is exposed. Uranium is a silver-colored metal which resembles nickel in appearance and is capable of taking a high polish. However, the metal surface oxidizes to a golden color after a few hours' exposure to air, and after several days the tarnish becomes dark brown. Uranium melts at about 1100°C. (2010°F.) and boils at about 4300°C. (7770°F.). Its density is almost 19 g./cu.cm. (1185 lb./cu.ft.) which is nearly twice that of lead and approximately the same as gold and tungsten. A solid cube of uranium with sides slightly over 14 in. long would weigh one ton.

When heated to about 170°C. in the presence of air uranium starts to burn. Thus, a vacuum or inert atmosphere is required for melting the metal. Finely divided uranium burns spontaneously in air and "sparks" when machined, sawed, or filed. Uranium in the finely divided form also slowly decomposes cold water. The rate of reaction becomes quite vigorous at the boiling point of water.

2. Chemistry of Uranium Dissolving

Uranium metal is dissolved and oxidized by nitric acid to uranyl nitrate, $UO_2(NO_3)_2$. Since uranyl nitrate crystallizes as the hexahydrate, $UO_2(NO_3)_2 \cdot 6H_2O$, uranyl nitrate solutions are sometimes referred to as uranyl nitrate hexahydrate (or UNH) solutions. The properties of UNH solutions are discussed in Chapter IV. Under conditions of normal dissolving, uranium is oxidized essentially quantitatively to the (VI) state by the strong oxidizing action of the nitric acid.

The rate of the uranium-dissolution reaction varies directly as the temperature and acid concentration. The following equations indicate the chemistry of the reactions:

$$U + 4HNO_3 \longrightarrow UO_2(NO_3)_2 + 2NO + 2H_2O$$

$$U + 8HNO_3 \longrightarrow UO_2(NO_3)_2 + 6NO_2 + 4H_2O.$$

Since in actual practice in the Bismuth Phosphate Plants it has been found that about 5.5 moles of acid are consumed per mole of uranium, the composite dissolution reaction at the boiling temperature, 101 to 108°C., may be expressed as:

$$U + 5.5HNO_3 \longrightarrow UO_2(NO_3)_2 + 2.25NO_2 + 1.25NO + 2.75H_2O.$$

The amount of nitric acid consumed depends upon the rate of removal of nitrogen gases, which, in turn, is a function of the design and operation of the Dissolver Column and the rate of air leakage into the Dissolver. Other variables affecting acid consumption are temperature and acid concentration. As indicated in the equations above, both NO and NO_2 are evolved when uranium is dissolved. In the presence of air

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which leaks into the Dissolver by virtue of the negative pressure maintained therein, most of the NO is oxidized to NO_2. A portion of the gaseous mixture is condensed by the condenser and refluxed down the column as nitric acid. The reflux tends to scrub the NO_2 from the rising gases.

The heat of formation of uranyl nitrate ranges from 1472 B.t.u./lb. at 18°C. for $UO_2(NO_3)_2$ to 2713 B.t.u./lb. at 18°C. for $UO_2(NO_3)_2 \cdot 6H_2O$. If the concentration of the acid charged is about 60% by weight or higher, the liberated heat is sufficient to keep the reacting mixture at the boiling point.

3. Chemistry of Plutonium Dissolving

The relatively small quantity of plutonium which has been formed from uranium in the piles is distributed throughout the slug. However, the concentration of the plutonium in the slug is not uniform, there being a concentration gradient from the outside of the slug to the core. Plutonium concentration near the slug core is approximately three quarters of that near the outside surfaces. Plutonium is oxidized by nitric acid during the dissolution step to either the (III) or (IV) oxidation state and forms soluble nitrates. Plutonium (IV) is the predominant state since Pu(III) is quite easily oxidized to Pu(IV) by the nitrite impurities always present in nitric acid. There has been no indication of any appreciable oxidation to the (VI) state. The dissolution reactions for plutonium are analogous to those for uranium. One reaction for the (IV) oxidation of plutonium may be written:

$$Pu + 8HNO_3 \longrightarrow Pu(NO_3)_4 + 4NO_2 + 4H_2O.$$

A more detailed treatment of plutonium oxidation is given in Subsection C2 which indicates that the equation listed above may represent a greatly simplified statement of the reaction.

Normally, Dissolver solution is slightly acidic after the dissolution reaction is arrested. However, dissolving to reduced residual acidities or to acid deficiency increases the likelihood of plutonium (IV) polymer formation. This possibility is discussed further in Subsection C2.

4. Distribution of Fission-Product Elements During Dissolution

Fission-product elements are present in the uranium slug in approximately the same total weight as plutonium when formed in the piles. As the slug "cools" the radioactive elements decay toward stable (i.e., non-radioactive) forms. The wide variety of the radioactive elements present includes species which are volatile, as well as species which are both soluble and insoluble in nitric acid.

The acid-soluble materials carry along with the uranium solution until selectively removed at subsequent points in the process.

The nitric acid-insoluble materials are present in very small quantities and do not necessitate special handling procedures for the uranium solution.

The volatile material of greatest importance is radioiodine. Radioxenon is present in smaller quantities; radiokrypton, in somewhat larger amounts; but they have less radiological importance since they do not tend to concentrate in living tissue as does iodine. Due to the long half life of krypton-85 (9.4 years), eventual slight contamination of the earth's atmosphere with this element may occur unless removal is ultimately effected. However, it would take the continuous development of about 10^5 megawatts of nuclear power to bring the atmosphere of the earth (assuming uniform dilution) to a concentration of krypton-85 equivalent to the activity associated with the radon and thoron naturally present in the atmosphere.(17) A proportion of all of the volatile elements appears in the Dissolver off-gas; about 50% of the iodine is liberated there. It is expected that a negligible proportion of the iodine will be liberated from the Oxidizer (since iodate formation is enhanced by the oxidizing conditions prevailing during ruthenium distillation). The fate of iodine during solvent-extraction is not known. The bulk of the iodine activity, because of the physiological hazard, should be removed before off-gas disposal to the atmosphere.

The following table lists approximate quantities of the important fission-product elements liberated during dissolving at 90 days after slug discharge from the piles:

Fission Element	Countable Curies	
	Beta Curies/Day	Gamma Curies/Day
I-131	1 to 5	2 to 10
Xe-133	0.5 to 2	0.5 to 2
Kr-85	100 to 300	

The quantity of iodine listed above is reduced by a factor of about 1000 by reaction with silver before being discharge to the atmosphere.

5. General Discussion

The normal Dissolver charge of 7700 lb. of uranium (about 1960 four-in. long slugs) is dissolved in three increments after slug jackets have been removed. A heel of about 2000 lb. of uranium normally remains in a Dissolver before charging of a new batch. Since the dissolution is chiefly a surface reaction, a more uniform surface-area relationship per cut exists if the heel of one charge, having a relatively small surface area, is held for the next charge. Attempts to dissolve to no heel would require too long a time due to the progressively smaller slug surface area presented to the nitric acid. Furthermore, since plutonium distribution throughout the slug is not uniform, maintaining a one-ton heel of core material in the Dissolver tends to equalize what might be even greater differences in the plutonium concentrations of each cut. Solution blending in storage tanks after discharge from the Dissolver also tends to minimize these differences.

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During the dissolution period about 1500 lb. of nitrogen oxides are evolved per 2600-lb. Dissolver cut. It is expected that radioiodine will be largely removed before the off-gas is discharged from the stack. Radioxenon and krypton content, on the other hand, will not be reduced, except for the effects of radioactive decay.

The rate of xenon evolution from the Dissolver is approximately proportional to the rate of the uranium-nitric acid reaction. The rate of iodine evolution indicates that once the Dissolver reaches the boiling point, the column reflux tends to scrub iodine out of the off-gas. When most of the acid has been consumed in dissolving, the acidity of the reflux falls off and iodine again leaks through the column. Evolution of radioactive gases essentially stops when the charge is diluted and cooled. The explanation of varying iodine concentration in dissolver off-gas has been checked by laboratory experiments during which it was found that iodine was lost from a refluxing solution of dilute nitric acid but not from a refluxing solution of strong acid.

In general, the first two Dissolver cuts require about the same length of time for completion. It is believed that the corroded and pitted slug surface at the start of the second cut has about the same surface area as the relatively smooth surface of the slug at the start of the first cut in spite of reduced slug size. The third cut requires more time than the first two (about 7 hours as compared to 6 hours) and reflects the decreased surface area due to still further reduced slug size. An increase in the amount of heel carried tends to increase the speed of the reaction.

The use of initial nitric acid concentrations below 60% by weight is not efficient because of the slow reaction rate. Acid strengths up to 70% have been used in semiworks studies on single batch charges. Higher acid concentrations increase the reaction rate but also increase the corrosion rate of the Dissolver. From the standpoint of both vessel corrosion and reaction rate, 70% nitric acid is the maximum acid strength permissible, and even this concentration is not recommended for multiple batch dissolving.

Dissolving is continued until a specific gravity of 1.82 (at boiling temperature) has been reached. This specific gravity indicates almost total consumption of nitric acid. Usually it is not possible to predict the composition of a three-component mixture (UNH-HNO_3-H_2O), but in this case, HNO_3 in the small residual quantities that remain has little effect on the specific gravity. Hence it is impossible to control nitric acid concentration in the UNH solution by means of specific gravity measurements near the point of zero acidity (0.2 M to -0.2 M HNO_3). Figure III-1 presents specific gravity of UNH solutions as a function of weight per cent of UNH at 0, 2, and 5 per cent free nitric acid concentrations.(7)

A water rinse solution is added to the slug heel in the Dissolver after transfer of the uranium solution. The rinse solution covers the heel until the succeeding charge is scheduled for loading into the Dissolver. This arrangement allows use of Dissolver-coil cooling water for removing the heat of radioactive decay.

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C. OXIDATION AND RUTHENIUM DISTILLATION

1. Introduction

The Redox IA Column is designed for the extraction of plutonium (VI) into the organic phase with a loss of less than 0.2% into the aqueous waste. Plutonium in freshly dissolved slug solution exists chiefly in the (IV) oxidation state. It is oxidized to the (VI) state in the Oxidizer, H-4. Enough holding oxidant (sodium dichromate) is maintained in solution to insure that the plutonium remains in the (VI) state until its extraction into the organic effluent stream of the IA Column.

Dissolver solution contains uranium as U(VI). This oxidation state extracts satisfactorily in the IA Column. Hence no specific preparation steps for uranium (other than concentration adjustment) are required prior to solvent-extraction.

Radioruthenium is limiting as far as decontamination of Redox product streams is concerned.(6) A significant gain in overall fission-product decontamination may be attained if the bulk of the ruthenium is removed from solution prior to feeding to the Extraction Battery. Most of the ruthenium may be distilled out of solution if it is oxidized to the volatile compound, ruthenium tetroxide (RuO_4). The sparging action of a carrier gas aids in carrying away the RuO_4.

Favorable results of head-end treatment methods (ruthenium removal plus niobium and zirconium scavenging, described under D3 below) may make possible the elimination of the third solvent-extraction decontamination cycle; very efficient head-end treatment brings nearer the attainment of required fission-product decontamination factors for product streams in a single extraction cycle.

First-cycle ruthenium decontamination may be improved by factors of 10 to 50 by utilization of a ruthenium distillation step. Gross fission-product decontamination is improved by factors of the same order of magnitude.(5) The distillation operation is accomplished in the Oxidizer more or less concurrently with plutonium oxidation procedures.

2. Plutonium Oxidation

2.1 Chemistry

Plutonium in solution may exist in the following states of oxidation, each of which exhibits a characteristic color: Pu(III), blue-violet; Pu(IV), brown-green; Pu(V), colorless; and Pu(VI), pink-orange.

The plutonium in dissolver solution is preponderantly in the Pu(IV) state if the normal dissolving techniques are employed. (See Section B, above.) Plutonium (III) also exists in dissolver solution, but it is rather readily converted to Pu(IV) in the presence of oxidants since only a single-electron transfer is involved.

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Aqueous nitrate complexes of Pu(IV) exist in acidic dissolver solution. The first reaction apparently is:

$$Pu^{+4} + NO_3^- \longrightarrow Pu(NO_3)^{+3}.$$

However, nitrate complexes up to and including $Pu(NO_3)_6^{-2}$ are probably present in stronger nitric acid solutions.(3)

Pu(IV) may also exist in the colloidal or polymeric state. The polymer seems to be a complex mixture of high-molecular-weight, hydrolyzed species of Pu(IV). Hydrolysis is believed to proceed stepwise by the addition of $(OH)^-$ groups to the Pu(IV) ion. The average formula of a high-molecular-weight polymer near a pH of 2 has been reported to be $Pu(OH)_{3.85}^{+0.15}$.(11)

Formation of a brown color in Pu(IV) solutions is indicative of the presence of the Pu(IV) polymer. The polymer is colloidal in nature, a rough estimate giving about 20,000,000 as the molecular weight and about 140 Angstrom units as the diameter of particles formed at a pH of about 1.7.(13) Usually the polymer is formed only at low acidities (0.1 M or less) or in basic solutions. Since the Dissolver solution will normally be about 0.2 M in nitric acid, the formation of the polymer should be largely avoided. If dissolving is carried to very low residual acidities or to acid deficiency it may be formed in considerable quantities. Because the polymer is relatively hard to oxidize and difficult to extract into hexone without oxidation, strenuous oxidation efforts, such as treating for 2 to 6 hours with 0.1 M sodium dichromate near boiling temperatures, might be required in the event of polymer formation.(21)

It has been shown that plutonium (V) and (VI) exist as the plutonyl ions PuO_2^+ and PuO_2^{++}. Electromotive-force measurements on cells containing Pu(IV) in disproportionation equilibrium are consistent with the following reaction:

$$3Pu^{+4} + 2H_2O \longrightarrow 2Pu^{+3} + PuO_2^{++} + 4H^+.$$

The oxygen-plutonium bonds in Pu(V) and Pu(VI) seem to be at least partially covalent in character. Thus, an oxidation or reduction of Pu(III) or (IV) to or from Pu(V) or (VI) involves the making or breaking of covalence bonds and not just simple electron transfers. A single-electron transfer is involved, on the other hand, in the oxidation or reduction reactions between Pu(III) and (IV) and between Pu(V) and (VI). These facts explain the relatively high rate of oxidation of Pu(III) to (IV) or Pu(V) to (VI) as compared to the oxidation of Pu(IV) to (VI), for example.

There is some evidence that Pu(VI) associates weakly with the nitrate ion at low acidities according to the following reactions:(4)

$$PuO_2^{++} + NO_3^- \longrightarrow PuO_2\,NO_3^+$$

$$PuO_2^{++} + 2NO_3^- \longrightarrow PuO_2\,(NO_3)_2.$$

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The extraction coefficient (i.e., phase-distribution ratio) of Pu(VI) into the organic phase in the extraction columns is nearly twice that of Pu(IV). The oxidation of plutonium to the (VI) state is required since the 1A Column is designed on the basis of Pu(VI) extraction.

2.2 Oxidation techniques

A number of oxidizing agents have been proved effective for the oxidation of plutonium to the Pu(VI) state. Among them are sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$), potassium permanganate ($KMnO_4$), ceric nitrate ($Ce(NO_3)_4$), and ozone (O_3).

The oxidation operation as carried out in the Oxidizer is related to the volatilization of ruthenium since the oxidation of plutonium by certain oxidizing agents also carries the ruthenium toward its (VIII) oxidation state and volatilization as ruthenium tetroxide (RuO_4).

Both potassium permanganate and sodium dichromate are added to the Oxidizer. Although the permanganate oxidizes plutonium to the (VI) state its chief purpose is the oxidation of ruthenium to its volatile tetroxide, RuO_4, and eventually the $KMnO_4$ is completely destroyed. Sodium dichromate is utilized in solution chiefly as a holding oxidant to maintain plutonium in its highest oxidation state, especially through the 1AF adjustment step where the solution is made acid deficient. If no holding oxidant were present at this point partial reduction of Pu(VI) to Pu(IV) would take place with the possible formation of the difficult-to-extract Pu(IV) polymer.

3. Ruthenium Distillation

3.1 General

Decontamination factors obtainable in both the uranium and plutonium extraction cycles of the Redox process are largely limited by the presence of radioruthenium. The ruthenium in the Dissolver solution produced from 90-day "cooled" uranium comprises about 5 to 8% of the total beta activity of the solution and approximately the same proportion of gamma activity. Although 95 per cent or more of the radioactive ruthenium present in the Dissolver solution generally favors the aqueous phase, on the order of 1 per cent of this ruthenium is present in a different form which exhibits an organic-to-aqueons phase-distribution ratio on the order of 1.0, or higher. This small fraction of the ruthenium extracts into the hexone, accompanying the uranium and plutonium, and hence limiting decontamination.

If no specific ruthenium-removal steps are accomplished prior to solvent-extraction, the proportion of total radioactivity due to ruthenium in the first-cycle uranium product stream rises (from 5 to 8% in the Dissolver solution) to about 80 to 90% for beta activity and about 65 to 75% for gamma activity. The proportion of ruthenium activity increases somewhat in the uranium product streams of subsequent cycles. The activity due to ruthenium in the first-cycle plutonium product stream amounts to about 60 to 70% of total beta and 25 to 35% of

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78

DECLASSIFIED

total gamma activity. These percentages also increase for the product streams of subsequent plutonium cycles.(20) If, then, some method for removing the major portion of ruthenium activity prior to solvent-extraction were available, the overall Redox fission-product decontamination factors could be considerably improved. Removal of ruthenium by oxidation to the volatile tetroxide (RuO_4) and stripping from solution by steam or air accomplishes this end.

In the course of investigations of the ruthenium-removal problem, it has been noted that at least three species of radioruthenium (which have been named A_1, A_2, and B) exist in dissolver solution.(28) These species exhibit different rates of oxidation and different phase-distribution ratios for solvent-extraction. The ruthenium composition of the solution is largely determined by its past history.

Laboratory results have shown that species A_1 and A_2, are the easiest species to oxidize and remove from solution.(28) The extraction coefficient for species B is about one fourth of the combined ruthenium (species A_1, A_2, and B) extraction coefficient for untreated dissolver solution. Thus, the removal of species A_1 and A_2, simultaneously, increases slightly the ruthenium decontamination attainable across the IA Column. However, all species, after extraction into the hexone phase, behave as if a small fraction of the ruthenium exhibits an organic-to-aqueons phase-distribution ratio of 1.0 or greater. At Redox process conditions the portion of ruthenium which favors the hexone phase (and hence does not decontaminate readily) is on the order of 1 per cent of the total ruthenium present. Ruthenium decontamination is thus limited by the presence of this "inextractable" (or more properly "unscrubbable") species. The behavior of ruthenium during solvent-extraction is treated further in Chapters IV and V.

Inasmuch as the nature of the ionic or molecular species in which ruthenium exists in dissolver solution has not been established, it is impossible to write a complete equation for the oxidation reaction. If the ruthenium oxidation state is (IV), as is generally assumed, a four-electron change is involved in the conversion to RuO_4. Consequently, the reaction is probably stepwise, with ruthenium (VI) as an intermediate.(28) The necessity for passing through such an intermediate oxidation state may be one of the factors responsible for certain phenomena such as the "induction period" described in Subsection 3.2.

A number of oxidizing agents were tested for effectiveness in oxidizing ruthenium to RuO_4. The most promising agents were found to be potassium permanganate ($KMnO_4$) and ozone (O_3). The use of each agent is discussed in more detail below.

3.2 Ruthenium distillation by means of ozone

Radioruthenium may be oxidized to the (VIII) state, as RuO_4, by sparging hot (90°C.) dissolver solution with ozone in an air carrier-gas stream at the rate of about 0.13 cu.ft./min. per gal. of solution. In general, the rate of RuO_4 formation and removal increases with solution temperature, ozone concentration and flow rate, and efficiency of ozone dispersion in solution. Preliminary results indicate no dependence on

DECLASSIFIED

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HNO_3 concentration in the range of ~0.15 M to 0.3 M.[29] Approximately 85 to 95% of the total ruthenium has been removed by ozonization in semiworks studies.[5]

During the sparging period the ozone seems to act, first, as a liquid-phase oxidant for ruthenium with liberation of RuO_4 and, second, as a gaseous-phase holding oxidant to minimize ruthenium reduction and deposition on equipment in contact with the gaseous phase.

The rate of ruthenium removal from solution is roughly proportional to the ozone concentration and rate of flow of the sparge gas. However, ozonization on a plant scale imposes a practical limit on concentration; it may be cheaper to sparge for a longer period with reduced ozone content in the air. Two weight percent ozone in air is a practicable rate for production use, and this concentration appears to be adequate for ruthenium oxidation and RuO_4 removal.

A definite period of time elapses between the start of the ozone sparge and evolution of RuO_4 in measurable quantities.[28] It has been postulated that this "induction period" is a measure of the time required to oxidize some of the other elements in solution. Perhaps as long as these impurities are present in their unoxidized states, any ruthenium compound intermediate in the formation of RuO_4 is reduced before it can be oxidized further and swept from solution as the volatile tetroxide.[28] Evidence supporting this explanation of the induction period is provided by results which indicate that induction time is inversely proportional to ozone concentration, and that a strong liquid-phase oxidizing agent may reduce induction time markedly. Simple ozone sparging of the dissolver solution has resulted in induction times of up to 20 hours in semiworks studies; however, the addition of small amounts (0.01 to 0.03 M) of a strong oxidizing agent such as potassium permanganate ($KMnO_4$) to the solution before sparging has reduced induction time to less than 2 minutes on a laboratory scale and less than 30 minutes on a semiworks scale.[4,28] On the other hand, substitution of $Na_2Cr_2O_7 \cdot 2H_2O$, a slightly weaker oxidizing agent than $KMnO_4$, seems to have no beneficial effect in shortening the induction period. (This would be expected if the induction period is caused, at least in part, by the chromic ion resulting from the corrosion of stainless steel.)

Once RuO_4 volatilization has begun, it proceeds at a rate peculiar to each of the three species of ruthenium. Species A_1 is most easily oxidized and removed; species A_2 is next; and species B is much the least easily oxidized and removed. The rate of ruthenium volatilization is reasonably uniform during species A_1 and A_2 removal but levels off markedly when the bulk of these two species is gone. However, since species A_1 and A_2 together comprise about 80 to 98% of the ruthenium, it appears desirable to discontinue further ruthenium volatilization once the leveling-off period is reached. Semiworks studies show a ruthenium-removal rate of about 15% per hour (after the end of the induction period) leveling off at about 85% removal for ozonization without $KMnO_4$ in solution. Ozonization of a feed solution with $KMnO_4$

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present results in a ruthenium-removal rate of about 40% per hour leveling off at about 95% removal.(4)

When an ozone-induced ruthenium-volatilization operation is employed, the ruthenium decontamination factor of the first-cycle product streams (IBP and ICU) is improved by factors ranging from 10 to 50 (semiworks results) or 100 to 500 (laboratory results) over those for a flowsheet which has no specific ruthenium-removal steps prior to solvent-extraction.(5,28) Gross fission-product decontamination is improved by factors of the same order of magnitude.

3.3 Ruthenium distillation by means of potassium permanganate

Potassium permanganate will readily oxidize ruthenium to ruthenium tetroxide. Three techniques which have been successfully demonstrated for ruthenium removal from solution by $KMnO_4$ oxidation are:

(a) sparging the approximately 0.03 to 0.08 M $KMnO_4$ solution with air or nitrogen at operating temperatures of 90 to 95°C.;
(b) sparging the approximately 0.03 to 0.08 M $KMnO_4$ solution with steam at the boiling point of the solution; and
(c) simple boiling of the approximately 0.03 to 0.08 M $KMnO_4$ solution.

In techniques (a) and (b), an adequate rate of sparging is about 0.13 cu.ft./min. per gal. of solution. In all three cases the volatilization operation may be continued until the rate of RuO_4 removal levels off, indicating practically complete species A_1 and A_2 removal.

Technique (a) and the use of an air spargant is preferred in the Redox Plant because of the condenser capacity limitation for the vapor mixture evolved. If techniques (b) or (c) were used, increased condenser capacity for the carrier gas (water vapor) might have to be provided.

Potassium permanganate is a better oxidant for dissolver solution than ozone alone and nearly or equally as good as the ozone-permanganate combination. This fact has been demonstrated during study of ozonization techniques where it was found that the long induction period before start of measurable RuO_4 evolution using ozone alone was shortened to a matter of minutes by making the solution 0.01 to 0.05 M in $KMnO_4$. In addition, the same short induction time and equally effective ruthenium removal has been demonstrated when using permanganate without ozone.(5) The overall time saving attainable by use of $KMnO_4$ is one of its chief advantages over use of ozone (in addition to eliminating the installation and operating costs of ozone-generating equipment).

In addition to the removal of RuO_4 from solution due to $KMnO_4$ oxidation, it is desirable to hinder potential gaseous-phase reduction which would deposit ruthenium in lines and equipment. In laboratory experiments on the 35-ml. scale, carried out at Hanford in stainless steel equipment, almost complete deposition of ruthenium in lines and equipment in contact with the gaseous phase was observed in $KMnO_4$ volatilizations made without ozone. In volatilizations made with ozone

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the deposition was slight. However, semiworks data (35-gal. scale), obtained at S.P.R.U., have indicated no significant difference in the deposition of ruthenium from the gas phase when $KMnO_4$ alone, ozone alone, or both $KMnO_4$ and ozone are employed. The S.P.R.U. studies did not prove the presence or absence of ruthenium deposition on tank or line surfaces in contact with the process liquids. The extent and nature of ruthenium deposition therefore remains controversial. However, even if all the ruthenium were deposited, an equilibrium activity concentration equal to about 6 to 7 times the total fission-product gamma activity charged per day to the Oxidizer would be approached.(31) Such an activity level would not alter shielding requirements as presently specified and designed into the Plant. It has been hypothesized that trace amounts of Mn_2O_7 in the gaseous phase may serve as a holding oxidant for RuO_4 (preventing total deposition) in the case of $KMnO_4$ oxidation.(28)

Experiments have indicated that, during the oxidation of many of the components of the solution and the evolution of RuO_4, a gradual reduction of Mn(VII) to Mn(IV) takes place. The degree of Mn(VII) reduction depends on the history and composition of the solution as well as on the specific oxidation techniques employed. The use of $KMnO_4$ as a ruthenium oxidant is desirable from another point of view since the reduced Mn(IV) ion forms manganese dioxide (MnO_2), a precipitate which acts as a scavenging agent for certain other fission-product elements, notably zirconium and niobium. This topic is discussed in detail in the succeeding section. Furthermore, if desired, Mn(VII) may be reduced to Mn(II) by the addition of excess chromic nitrate to avoid the formation of a precipitate.

When a permanganate-induced ruthenium volatilization operation is employed, the ruthenium decontamination factors of the first-cycle product streams (IBP and ICU) are each improved by a factor of about 20 to 50 (semiworks results) over a flowsheet which has no specific ruthenium-removal steps prior to solvent extraction. Gross fission-product decontamination is improved by approximately the same amount.(5)

D. CLARIFICATION AND SCAVENGING

1. Introduction

The uranyl nitrate solution produced by dissolving irradiated slugs contains small amounts of suspended solids. These particles are mainly silicious in nature but also contain considerable quantities of tin in the form of metastannic acid. The silicon is partially in the form of metasilicic acid and partially as elemental silicon. Trace amounts of other elements are found in the particles. The solids apparently originate from bonding material between the uranium slug and aluminum jacket.

The presence of the suspended solid particles beyond certain tolerance amounts appears to make phase separation in the Extraction Battery more difficult as determined by phase disengagement time studies.

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In addition, potential deposition of the solids on Extraction Battery packing might ultimately lower column throughput capacities and make necessary special flushing procedures. It is possible that solids accumulation might eventually impair the operation of flow-measuring and flow-control devices.

Several methods for clarifying dissolver solution by removal of some of the suspended solids are available. They are included in two major classifications according to process, as follows:

(a) filtration, either with or without filter aids; and
(b) centrifugation, either with or without scavenging agents.

Filtration without filter aid has proved unsatisfactory because some of the solids are gelatinous and tend to plug the pores of the filter media. Filtration with a filter aid such as Super Filtrol F.O., an activated clay, has generally proved satisfactory for solids removal.(19)

Centrifugation is favored over filtration for solids removal since fewer mechanical difficulties are anticipated on a plant scale. If a scavenging agent is used, many of the fine suspended solids in solution may be intercepted by particles of the scavenger with a resultant improvement in the ease of solid-liquid phase separation (provided the scavenger itself does not contain large amounts of fines of the same size range as the suspended solids). Without a scavenger a longer time of solution holdup in the centrifuge bowl is required to achieve the same degree of suspended-solids separation.

The use of a scavenging agent to aid in solids removal during centrifugation offers another advantage. It has been demonstrated that radiozirconium and niobium (radioelements which, next to ruthenium, are major fission-product constituents of the Redox product streams) are adsorbed on certain scavengers and may be selectively removed when the scavenger is separated from the solution. Efficient adsorption of zirconium and niobium together with adequate ruthenium removal by distillation (as described in the preceding section) brings nearer the attainment of required fission-product decontamination factors for product streams in one extraction cycle and may, in any event, eliminate the need for using the third solvent-extraction decontamination cycle.

A number of materials have been tested for value as filter aids or scavenging agents. Most important among them are "Super Filtrol F.O." and manganese dioxide. Super Filtrol F.O., a commercial product, adsorbs up to about 99% of the zirconium and approximately 80% of the niobium, with proper operational techniques, in addition to its good efficiency as a filter aid for silicious particle removal. A disadvantage of using Filtrol in the plant is that it is a relatively insoluble solid, and must be handled in slurry form.

A fine precipitate of manganese dioxide may be formed in the dissolver solution by reduction of the permanganate ion. Manganese dioxide, too, acts as an efficient scavenger for niobium and zirconium. One of the important advantages of manganese dioxide as a scavenger results from the

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fact that the solid phase can be dissolved after separation from the liquid. The resulting waste solution may be handled much more conveniently than can a slurry.

2. Clarification

Clarification, as a term applied to oxidized dissolver solution, implies the partial removal of suspended particles from solution. An arbitrary procedure for clarity measurements involves comparison of the degree of transmission of 645 millimicron wave-length light by the sample with the light transmitted by distilled water.(19)

The exact process significance of dissolver-solution clarity is difficult to establish positively. In some degree it is a measure of the relative ease with which the organic and aqueous phases disengage in the extraction column. An increase in disengaging time generally indicates an increasing tendency toward emulsification. But there has been some evidence that emulsification can occur even with feed solutions whose clarities would normally be considered satisfactory (about 90% of the light transmission of the distilled water standard). Presumably, this condition is caused by polymers of metasilicic acid passing the centrifuge.(16)

The emulsification characteristics of dissolver solution seem to be chiefly a function of silicon content. Silicon concentrations in the vicinity of 60 p.p.m. may cause emulsification; those about 30 p.p.m. or less usually do not. The silicon content of the bonding material between slug and jacket averages about 5000 p.p.m. of the uranium in the slug while the silicon impurity in the uranium usually is in the range of 20 to 170 p.p.m.(18)

A higher than normal silicon content of dissolver solution may result from (a) greater than average silicon content in the uranium, (b) contamination of the dissolved uranium with silicon from the bonding layer between the slugs and their aluminum cans, or (c) silicon picked up by the solution from high-silicon sludge which may accumulate in the dissolver. These conditions leading to excessive silicon in the dissolver solution must usually be associated with less effective suspended-particle removal in the centrifugation operation in order to have silicon in the feed solution in sufficient quantities to cause emulsification.

In most cases, the tendency toward emulsification decreases as suspended particles are removed. Experiments have shown, however, that not all solid particles have the same effect in the inclination toward producing emulsification. Thus it is decidedly possible for a feed solution to exhibit less-pronounced emulsification characteristics after a centrifugation with a scavenger although there may be no net improvement in clarity. Presumably some of the original suspended solids have been replaced with fines from the scavenger which carry over into the centrifuge effluent.

The Redox Plant provides a Centrifuge through which oxidized Dissolver solution is routed. The Centrifuge bowl diameter is

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40 inches and it has a running holdup of about 60 gal. of solution. The Centrifuge will rotate at a speed of either 870 or 1740 rev./min.; these speeds produce, respectively, a centrifugal force at the bowl wall of 430 and 1730 times the force of gravity. The speed of 1740 rev./min. is required for a reasonable degree of suspended-particle removal, i.e., improving the clarity of the solution from about 75% to about 90% (distilled water standard).(25)

It would be expected that centrifugation without a scavenging agent in solution would remove some of the larger solid particles and hence improve clarity. Furthermore, with a scavenger even more of the solids should be adsorbed or screened out. Both of these conclusions are supported by experimental evidence. Use of a scavenger, however, may add fines to solution due to carry-over of the scavenger fines from centrifugation.

A running holdup time in the Centrifuge bowl of twenty minutes minimum should be maintained for Super Filtrol scavenger-containing solution in order to attain adequate solid-phase separation.(25) Holdup times should be somewhat longer if no scavenging agent is used. Increase of centrifugal force, whether or not scavenger is used, increases the rate of solid-liquid phase separation and hence improves ultimate clarity.

In addition to holdup time and centrifugal force, a third variable, quantity of scavenger per unit volume of solution, is available if a scavenging agent is used. Increasing quantities of Super Filtrol scavenger, up to a limit of about 2% by weight, improve clarity. Amounts of Super Filtrol in excess of 2% by weight seem to have no further beneficial action on clarity, and in some instances the effect may be slightly detrimental.(25)

Dissolver-solution clarification and the selective scavenging of niobium and zirconium are operations difficult to segregate since any scavenging agent utilized specifically for niobium and zirconium adsorption will also act as a scavenging agent for suspended-solid particle removal.

Subsection D3, below, discusses scavenging in reference to fission-product adsorption and should be considered together with this section.

3. Scavenging of Zirconium and Niobium

3.1 Scavenging with Super Filtrol F.O.

Super Filtrol F.O. is an activated clay consisting chiefly of SiO_2 and Al_2O_3. It is the trade name of a product of the Filtrol Corporation. The individual particles of Super Filtrol F.O. range in size downward from that just passing through 100-mesh screen (150 microns) to a size in the range of 0 to 20 microns. About half of the Filtrol (by weight) is in the 0 to 20-micron size range. Filtrol exhibits the property of adsorbing a high proportion of the zirconium and niobium from oxidized dissolver solution. Small amounts of other fission products

are adsorbed, but the adsorption of zirconium and niobium is most important since the activity due to these elements constitutes a major portion (after ruthenium) of the activity in Redox product streams.

The table below gives approximate quantities of zirconium and niobium present in dissolver solution at 90 days age:(20)

Fission Element	Countable Curies	
	Beta Curies/Day	Gamma Curies/Day
Zirconium	8000 to 12,000	20,000 to 30,000
Niobium	2000 to 4000	40,000 to 60,000

The adsorption efficiencies of the scavenger are apparently increased with increasing temperature; they seem to be independent of the age of the dissolver solution. A Filtrol scavenger concentration of about 60 grams/liter in hot (100°C.), oxidized dissolver solution will adsorb on the order of 97 to 99% of the zirconium and about 70 to 80% of the niobium. The adsorption efficiency seems to be independent of acidity in the pH range -0.3 to 1.4.(21) Multiple contacts of this scavenger totaling 60 grams/liter will equal or improve these figures. A Filtrol concentration of 60 grams/liter produces a volume of filter cake that is inconvenient to process in the Plant Centrifuge; 20 grams/liter (about 1.2% by weight) of Filtrol is about the maximum concentration permissible. Data indicate that scavenging efficiency is about 10% less for a 20 grams/liter scavenger-solution contact than for a 60 grams/liter contact.

Plutonium (IV) is adsorbed strongly (50 to 80% removal) in the hot (90 to 100°C.) digestion that is most beneficial to zirconium and niobium adsorption. But plutonium (VI) is not adsorbed to any appreciable extent. In order to avoid high plutonium losses on the scavenger, then, plutonium must be present in its most highly oxidized state. If plutonium (IV) is in solution and is adsorbed, lengthy, hot (90 to 100°C.) oxidation efforts are required to remove it from the scavenger. Such strenuous oxidation also removes 2 to 4% of the niobium and zirconium.

Filtrol scavenger at a temperature of about 50 to 60°C. is separated from the supernate liquor in the centrifuge. The resulting centrifuge cake is about 70 to 80 volume per cent liquid and has an apparent density of about 1.9 g./ml. Although plutonium (VI) is not adsorbed by the cake, enough plutonium and uranium are retained in the solution held up by the cake to be intolerable from a plutonium and uranium loss standpoint (0.1% limit). The cake may be easily slurried from the sides of the bowl with a wash solution, centrifuged, rewashed and recentrifuged until the dilution effect of the washes has reduced the plutonium and uranium losses to less than 0.1 per cent. Laboratory results have indicated no significant deviations from the laws of dilution; however, cake-washing effectiveness seems to be, to a minor degree, a function of the nitric acid concentration of the wash solution.(21) Experiments have shown

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that plutonium is removed more readily with increasing acid concentration. However, the degree of zirconium removal from the scavenger also increases with increasing acid concentration.

The following table presents quantitative data obtained in the laboratory:(21)

Wash Solution	Per Cent Removed from Cake After Centrifugation and Four Cake Washes	
	Pu	Zr
H_2O	99.71	2.8
0.01 M HNO_3	99.87	2.6
0.05 M HNO_3	99.88	3.2
0.10 M HNO_3	99.96	4.3

A balance between these factors indicates a wash solution 0.01 M in nitric acid as a good compromise.

The washed cake may be slurried from the centrifuge bowl by adding slurry water in an amount such that the Filtrol comprises no more than about 20% of the total slurry weight.(22) A Filtrol slurry of this composition exhibits satisfactory flow characteristics; i.e., it can be pumped or jetted like a liquid. Its apparent viscosity ranges from a minimum of about 1.8 centipoises at a velocity of 1.6 ft./sec. to about 4 centipoises at 3.7 ft./sec. Slurries with lower concentrations of Filtrol are less viscous, approaching the viscosity of water as a limit.(22)

3.2 Scavenging with co-formed manganese dioxide

If potassium permanganate is used as an oxidant during the ruthenium-distillation operations (see under C3.3) it is possible to co-form manganese dioxide scavenger in the Oxidizer by reduction of the permanganate. The extremely fine precipitate of manganese dioxide is an efficient adsorber of zirconium and niobium. It also adsorbs varying amounts of other fission-product elements. A manganese dioxide scavenger concentration of about 6.5 grams/liter in hot (100°C.), oxidized dissolver solution adsorbed on the order of 90 to 99% of the zirconium and niobium in laboratory studies(30), and about 90 to 99% zirconium, 90% niobium, 20 to 40% cerium, and about 1 to 10% of the original ruthenium in semiworks studies.(4,5) Multiple contacts of scavenger totaling about 10 grams/liter indicate laboratory adsorption efficiencies in excess of 99% for both zirconium and niobium.(30) If the manganese dioxide cake is subjected to prolonged heating (or standing at room temperature in the absence of permanganate for periods greater than a few hours) a portion of the ruthenium and zirconium scavenged is desorbed.(5) However, the ruthenium species removed is apparently solvent-insoluble and does not significantly affect the overall ruthenium decontamination adversely.

During ruthenium volatilization, some $KMnO_4$ is reduced by virtue of the oxidation of many of the components of dissolver solution, and MnO_2 is produced. The stability of $KMnO_4$ during ruthenium distillation is anomalous, and the amount of MnO_2 formed has not been correlated with any solution variable.

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In the chromic-strike method of precipitating MnO_2, residual Mn(VII) as $KMnO_4$ is reduced to Mn(IV) as MnO_2 by the addition of chromic nitrate according to the following reaction:

$$2KMnO_4 + 2Cr(NO_3)_3 + 3H_2O \longrightarrow 2MnO_2 + K_2Cr_2O_7 + 6HNO_3.$$

In the manganous-strike method, residual Mn(VII) is reduced to Mn(IV) by the addition of Mn(II) as manganous nitrate according to the following reaction:

$$2KMnO_4 + 3Mn(NO_3)_2 + 2H_2O \longrightarrow 5MnO_2 + 4HNO_3 + 2KNO_3.$$

In practice this reaction requires somewhat more than the stoichiometric quantity of $Mn(NO_3)_2$. Experiments have shown that any dichromate ion present in solution (as a holding oxidant for plutonium) is not reduced in appreciable quantities by the reducing action of Mn(II). In fact, as discussed in Subsection D4, the reduction potential of Cr(III) is sufficient to reduce MnO_2 to Mn(II). The reducing action of Cr(III) on Mn(VII), of course, simultaneously oxidizes the Cr(III) to Cr(VI) as dichromate.

Both the chromic-strike and the manganous-strike methods for permanganate reduction may be accomplished by "fast strike" or "slow strike" procedures. In the fast strike procedure, permanganate reduction and MnO_2 digestion is carried out in a 30-minute period at a temperature of about 75°C. In the slow strike procedure, reduction begins at 30°C. and takes place during a 30-minute period while heating at the rate of 1°C. per minute. A 30-minute digestion at 75°C. completes the procedure. It was thought that efforts to produce larger particle sizes by the slow strike methods would be beneficial to ease of handling in the centrifugation step. There appear, however, to be no differences in either adsorption efficiency or handling ease between precipitates produced by slow or fast strike methods.

The MnO_2, containing adsorbed fission products, is separated from the supernate liquor in the Centrifuge. The MnO_2 cake holds up more liquid (about 90 to 99 volume per cent) than does Super Filtrol F.O. The cake is less dense than that of Filtrol; the apparent density may range from about 1.7 to 1.9 g./ml. The MnO_2 cake is somewhat more greasy and sticky than that of Filtrol, but nevertheless it is easily slurried down from the bowl wall by the impinging action of wash solution from the bowl sprays.

It is believed that MnO_2 will oxidize Pu(IV) to (VI) in case any Pu(IV) is present in solution during scavenging (not a normal condition) This should preclude any potential adsorption of Pu(IV) on the cake. The same washing techniques described for Filtrol for recovery of uranium and plutonium in the cake liquor also apply to the MnO_2 cake.

One of the chief advantages of MnO_2 scavenger over Filtrol is the fact that the washed cake may be dissolved by reducing Mn(IV) to Mn(II). The objectionable features inherent in the handling and disposal of a slurry are eliminated. One method of cake dissolution involves treatment with dilute hydrogen peroxide in acid solution according to the

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following reaction:

$$MnO_2 + H_2O_2 + 2HNO_3 \longrightarrow 2H_2O + O_2 + Mn(NO_3)_2.$$

The catalytic action of MnO_2 on H_2O_2 decomposition has been known for many years. Because of the instability of H_2O_2 about 100% excess is required for the manganese dioxide dissolution reaction. The concentration of H_2O_2 in the solution added for cake dissolving should not be greater than about 10% since in higher concentrations H_2O_2 decomposition by MnO_2 catalysis is too vigorous.

Any strong reducing agent that does not form a precipitate as a reaction product should serve adequately as a MnO_2 cake dissolver. The use of Fe(II) has been suggested. Such a reaction would proceed in the following manner:

$$2\ Fe^{++} + MnO_2 + 4H^+ \longrightarrow Mn^{++} + 2\ Fe^{+++} + 2H_2O.$$

A 20% ferrous sulfamate, 10% HNO_3 solution has been successfully used for dissolving the cake. Because of the greater solution stability it is preferred over H_2O_2 cake dissolution methods.

MnO_2 may be reduced by an excess of Cr(III) in the following manner:

$$2Cr^{+++} + 3MnO_2 + H_2O \longrightarrow 3Mn^{++} + H_2Cr_2O_7.$$
(50% excess)

Since the dissolved cake solution is stored underground without additional processing, the nature of the ions introduced for cake dissolution is relatively unimportant.

4. Centrifugation Without Scavenging

The use of scavenging procedures for selective removal of large proportions of zirconium and niobium and lesser amounts of other fission-product elements depends largely on an economic balance between costs of the operations and savings that may result from them. In the event that scavenging is not deemed advisable, the permanganate used for ruthenium distillation may be reduced through the Mn(IV) state (MnO_2) to the soluble Mn(II) state. If an excess of chromic nitrate is added to the oxidized dissolver solution both the residual Mn(VII), as $KMnO_4$, and the Mn(IV), as MnO_2 precipitated during sparging, will be reduced th the soluble manganous nitrate. Two moles of chromic nitrate per mole of $KMnO_4$ plus one mole per mole of MnO_2 are sufficient to accomplish the reduction. The reactions may be summarized as:

$$10Cr(NO_3)_3 + 6KMnO_4 + 11H_2O \longrightarrow 6Mn(NO_3)_2 + 3K_2Cr_2O_7 + 18HNO_3 + 2H_2Cr_2O_7$$
(20% excess)

$$2Cr(NO_3)_3 + 3MnO_2 + H_2O \longrightarrow 3Mn(NO_3)_2 + H_2Cr_2O_7.$$
(50% excess)

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The centrifugation operation would still remove significant amounts of the silicious dissolver-solution solids with no scavenger present. It is likely that more of the very small particles would pass through the centrifuge, however, although increasing the solution holdup time in the centrifuge bowl tends to improve solids removal. If adequate silicious-particle removal can be obtained without scavenging, it may be economical to abandon the scavenging operation.

E. IAF ADJUSTMENT

1. General

The centrifuged Dissolver solution corresponds roughly to the flowsheet IAF composition (2.0 M UNH, 0.1 M $Na_2Cr_2O_7$, -0.2 M HNO_3, and 0.38 M $NaNO_3$). The centrifuged solution is, however, slightly more concentrated in uranium and oxidizing agent than the flowsheet IAF, and in addition contains about 1% by weight of HNO_3. The acid has resulted from the small excess used in the slug-dissolving step to prevent formation of difficult-to-extract plutonium complexes.

The operation of neutralizing the acid and producing the required state of "acid deficiency" (-0.2 M HNO_3), and then adjusting, by dilution, final solution composition to that of IAF is carried out in the IAF Make-Up Tank. This vessel also serves as the centrifugate catch tank. After adjustment, the IAF solution is batch-transferred to the IA Feed Tank which continuously feeds the uranium-plutonium-fission-product stream to the IA Column. Further discussion regarding the specified flowsheet concentrations are found in Chapter IV.

2. Acid Deficiency

The IAF solution containing -0.2 M HNO_3 (0.2 M HNO_3 acid deficient) would become stoichiometrically neutral upon addition of 0.2 moles of HNO_3 per liter of solution. The pH of the solution, however, is still on the acid side (approximately 2). Acid deficiency is discussed further in Chapter VIII. Decontamination in the IA Column is markedly improved with an acid-deficient feed as compared to a feed slightly acidic. Most of the improvement is traceable to much-improved ruthenium decontamination with no important adverse effects on decontamination from other fission-product elements.

3. Methods

The centrifuged feed solution as received in the IAF Make-Up Tank contains plutonium and uranium in the (VI) oxidation state. Sodium dichromate is present in solution (in about 0.1 M concentration) as a holding oxidant for plutonium, since it is necessary that plutonium be maintained in the (VI) oxidation state in the IA Column in order to achieve satisfactory plutonium extraction (less than 0.2% loss into the IAW aqueous effluent stream). Without the presence of a holding oxidant, the reduction of plutonium (VI) to (IV) during the operation of making the solution acid deficient is a possibility.

The slight acidity in the centrifuged feed solution (approximately 0.2 M HNO_3) is neutralized and the required state of acid deficiency is produced by the addition of a sodium hydroxide solution (25%).

Final concentration adjustment is accomplished by dilution of the batch to the required final volume.

F. GAS TREATMENT

1. General

Gaseous wastes from the Redox Plant consist of canyon, silo, and cell ventilation air; air or nitrogen discharged from the various equipment vent headers; and any gaseous products formed as a result of a process operation. The latter group is the most important in that treatment methods required to ready the gases for discharge into the atmosphere are more elaborate because of the higher proportion of radioactivity involved.

Canyon, silo, and cell ventilation air is filtered by a graduated gravel and sand filter bed where radioactive particles in the air are intercepted by the filter media.

Discharge gas from the vent headers passes through capsule-type Fiberglas filter units where, again, radioactive particles are intercepted by the fibers of the filter.

The gaseous reaction products of greatest importance are those formed in dissolving uranium metal and those formed in oxidizing the uranium solution. Both are treated in more detail in subsequent parts of this section. In general, one or more specific operations is applied to each and the exit gas from each special treatment is routed through a Fiberglas filter.

All three general types of gaseous products are discharged into the atmosphere through the Stack after passing their respective filters. Reference is made to Chapter X for a detailed discussion of gaseous waste disposal and the functions of the Stack and filter units.

2. Removal of Iodine with Silver Reactor

The chemical nature of dissolver off-gas has been mentioned previously in this chapter. Although radioiodine-131 has a relatively short half life (about 8 days), it is still highly important as one of the elements of the off-gas because of its tendency to concentrate in plant and animal tissues if allowed to pass into the atmosphere. The radioactive isotopes of two gases, xenon and krypton, contribute the bulk of the remaining fission-product radioactivity to the off-gas stream. These elements are usually of little concern from the physiological point of view since:

(a) being inert, they are not concentrated in living tissue;
(b) being gaseous under atmospheric conditions, they do not tend to deposit out of the atmosphere, but are more or less uniformly diluted.

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The half life of xenon-133 is about 5.3 days; hence xenon soon decays to innocuous values after discharge into the atmosphere. Krypton-85, on the other hand, has a half life of about 9.4 years, and if discharge of krypton were to continue indefinitely very slight contamination of the earth's atmosphere would ultimately result (see Subsection B4).

The Redox Plant will be provided with Silver Reactors for removal of iodine from the Dissolver off-gases. Gaseous iodine will react with hot silver or silver nitrate very rapidly when passed over the surface of the solid. Iodine reactivity is increased with temperature. The very high removal efficiency of iodine by hot silver is probably due, in part, to the low vapor pressure of iodine above silver iodide at operating temperatures. The equation for the reaction is:

$$I_2 + 2Ag \longrightarrow 2AgI.$$

Silver nitrate-coated packing is used for reaction with iodine. The exact reaction mechanism is not known with surety but may be represented by the usual iodine reaction in the presence of an excess of silver nitrate:

$$6AgNO_3 + 3I_2 + 3H_2O \longrightarrow 5AgI + AgIO_3 + 6HNO_3.$$

There may be some $AgNO_3$ dissociation under operating conditions so that the following series of reactions may occur to a limited degree:

$$2AgNO_3 \longrightarrow 2AgNO_2 + O_2, \quad 2AgNO_2 \longrightarrow 2Ag + 2NO_2, \quad 2Ag + I_2 \longrightarrow 2AgI.$$

Performance data on a small-scale silver reactor (2-in. diameter unit packed with 1 in. of 1/4-in. silver nitrate-coated Berl saddles) have indicated high iodine-removal efficiencies for even this relatively shallow packing layer when dissolver off-gases were passed through the unit at a rate of about 2 cu.ft./min. The efficiency of the unit as a function of the temperature of the packing bed is:(26)

Temperature of Bed, °F.	Per Cent of Iodine Removed
260	95.8
620	96.7
820	97.3

The $BiPO_4$ Plant Silver Reactor, installed in 221-B canyon, is 2 ft. in diameter and is packed to a depth of 8 ft. with 1/2-in. silver nitrate-coated ceramic Berl saddles. When the entire volume of dissolver off-gases is passed through this unit, the vapor velocity in the Reactor is approximately the same as that employed in the small-scale tests which were described above. At an average inlet off-gas temperature of 475°F. (exit off-gas temperature is about 300°F.), the iodine-removal efficiency of the Reactor has been 99.9%. The precision of sampling and analytical techniques prevent the determination of a fourth significant figure.(32)

As inferred from the small-scale studies, most of the iodine is removed in the first inch or two of packing. Data indicate that the

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efficiency of iodine removal remains at a high level (95 to 99+%) until the silver available for reaction in this packed depth is about 40 to 50% depleted.(1) When these data are extrapolated to plant-scale dissolving conditions the theoretical life of the test unit in 221-B, based on available silver, is on the order of 10 to 15 years. Secondary effects such as spalling of the ceramic packing, passivation of the reactive surfaces, or increased pressure drop may reduce the duration of high-efficiency operation to one to two years. The Redox Silver Reactor is the operational equivalent of the 221-B unit.(10)

The temperature of the gases entering the Silver Reactor should be controlled at between 450 and 500°F. (which maintains exit gas temperature at about 300°F.) for the following reasons, in addition to high iodine-removal efficiency at this elevated temperature:

(a) At temperatures permitting condensation (less than 220°F.), the rate of iodine removal decreases markedly. Appreciable condensation would remove silver nitrate by solution.
(b) At gas inlet temperatures above 500°F., the silver nitrate starts to soften, becoming noticeably fluid (viscous) at about 550°F., and quite fluid at 600°F.(10) (Even with gas inlet temperatures of 450 to 500°F. the silver nitrate on a short section of packing near the inlet may melt, but the viscous, molten silver nitrate remains on the surface of the packing.)

3. Scrubbing of Dissolver Off-Gas

At this writing, plans are under way to employ the Silver Reactor as the means of removing radioiodine from Dissolver off-gas. Originally it had been planned to accomplish this, together with removal of oxides of nitrogen, by scrubbing the off-gas with a caustic solution in Off-Gas Scrubbers. Means will yet be available for carrying out caustic scrubbing following the Silver Reactor. Stub connections have been provided in the off-gas lines for the later insertion of caustic scrubbers if desired.

Since most of the NO in the off-gas is oxidized to NO_2 in the presence of an excess of air (there are about 3 volumes of air per volume of off-gases) the reaction of the nitrogen oxides with caustic becomes:

$$2NO_2 + 2NaOH \longrightarrow NaNO_3 + NaNO_2 + H_2O.$$

Radioiodine reacts with the caustic according to the following reaction:

$$2NaOH + I_2 \longrightarrow NaI + NaOI + H_2O.$$

Evidence indicates that the sodium hypoiodite dissociates quite rapidly in the following manner:

$$3NaOI \longrightarrow NaIO_3 + 2NaI.$$

Then the composite reaction may be written as:

$$6NaOH + 3I_2 \longrightarrow NaIO_3 + 5NaI + 3H_2O.$$

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Nearly the entire original amounts of radioxenon and krypton in the Dissolver off-gas pass through the Off-Gas Scrubber and are emitted from the Stack.

When the NO_2 reacts with NaOH, heat is liberated at the rate of about 45,000 Btu/lb. mole of NO_2. The average rate of NO_2 reaction with NaOH in the Off-Gas Scrubber is about 6 to 7 lb. moles per hour during a 6-hour dissolving period. The evolution of such large amounts of heat necessitates either the use of a large excess of caustic to carry away the heat of reaction, or a recirculating system with the heat transferred to cooling water in a heat exchanger. The Off-Gas Scrubber utilizes the latter method. The result is that the ascending vapors in the Scrubber column are contacted by a solution consisting of about 19% $NaNO_2$ and 27% $NaNO_3$ and enough free caustic (about 6%) to provide a sufficient amount for the NO_2 reaction. This amount of free caustic is equivalent to about 20 lb. moles per hour, enough to react with about 3 times the average quantity of NO_2 evolved per hour. It is anticipated that the maximum rate of NO_2 evolution will be no more than 3 times the average rate.

Since most of the activity associated with Off-Gas Scrubber aqueous waste is due to radioiodine, and since the half life of this element is about 8 days, it may be feasible to crib the waste after about one-half to one year's decay time in the Underground Cascade. Eventual cribbing may be possible only if long-lived fission products reach the Scrubber wastes in very minute amounts and no other process wastes are routed to the Cascade which receives from the Off-Gas Scrubbers.

4. Scrubbing of Ruthenium Tetroxide

The hot gases passing into the Ruthenium Scrubber from the Oxidizer contain ruthenium activity in the form of a volatile compound, ruthenium tetroxide (RuO_4). Large amounts of an inert carrier gas serve as the sweeping agent for RuO_4 removal from the Oxidizer. Only trace amounts of fission products other than ruthenium are present in the carrier gas.

The absolute quantity of ruthenium in the gas is quite small, on the order of 2 to 3 grams per day. About 7000 to 8000 beta curies and 5000 to 6000 gamma curies of activity are associated with this quantity of ruthenium at 90 days' age.(20)

Laboratory tests have shown the removal of RuO_4 by absorption in a caustic solution to be quite rapid.(28) Consequently, a 25% caustic solution is employed as the recirculating scrubbing liquid for the Oxidizer off-gas. The exact absorption mechanism is unknown; however, it has generally been assumed that Ru(VIII) is reduced to Ru(VI) as the soluble ruthenate salt, Na_2RuO_4.

Slight amounts (on the order of 50 mg./l. or less) of sodium ruthenate in the caustic solution produce a weak orange color which is indicative of the presence of this salt.

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Batch laboratory results indicate slightly more efficient ruthenium tetroxide absorption in 3 M sodium hydroxide solution at room temperature than at 95 to 100°C.(28) It is necessary that the Ruthenium Scrubber be operated at a temperature of about 90 to 95°C. (to avoid condensation in the Scrubber of large amounts of water vapor in the carrier gas); however, insignificant ruthenium loss is expected because of the small absolute quantities involved and the demonstrated effectiveness of the scrubbing. Semiworks studies have indicated that less than 0.001% of the ruthenium passes a recirculating caustic absorbing stream.

G. PROCEDURE

1. Normal Procedure

1.1 General

The Redox Plant is designed on the basis of a nominal uranium processing rate of 2-1/2 tons/day. Since the design was based on an assumed time efficiency of 80% (operating time is 80% of actual time), the nominal instantaneous rate becomes 3-1/8 tons of uranium/day. Figure III-2 shows a Material Balance Flowsheet and III-3 an Engineers' Flow Sketch for the Uranium Feed Preparation portion of the Redox process. The oxidation and centrifugation steps of Figure III-2 are based upon permanganate oxidation for the distillation of ruthenium and upon co-formation of manganese dioxide scavenger by means of the chromic nitrate strike for reduction of residual permanganate for scavenging of zirconium and niobium. As indicated in Sections C and D, alternative procedures might be employed. Figure III-3 shows the equipment provided and line routings available for the Redox process and will be referred to in connection with the following discussion.

1.2 Coating removal and dissolving

Three Dissolver groups have been provided in the Redox Plant. Normally only two Dissolvers are required in order to maintain the basic production rate. The third unit serves as a spare or may be used together with the other two to rapidly build up a uranium-solution inventory when required. Each of the three Dissolver units is complete in itself and consists of a Dissolver, Rinse Tank, Off-Gas Heater, Silver Reactor, Off-Gas Filter, Dissolver Drowning Tank, and Dissolver Large and Small Weigh Tanks. Reference is made to Figure III-3 for equipment grouping and line routings.

A basis charge to a Dissolver consists of 7700 lb. of uranium (about 1960 four-in. long slugs) in irradiated, jacketed-slug form. The slug-handling procedures, through the loading of a slug charge into a Dissolver, are described in Chapter II; the Dissolvers are described in Chapter XIII. The following discussion applies specifically to the A-Cell Dissolver, A-2, but is equally applicable to any of the Dissolver units.

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A heel of about one ton of uranium is normally carried in the Dissolver and the new charge is dropped on the heel. Approximately 4950 lb. of 26% sodium nitrate solution is added to the Dissolver from Large Weigh Tank A-2-A and the solution is heated to boiling with the coil and sparger. The Dissolver is maintained at 20 to 30 inches of water negative pressure during jacket-removal operations to prevent the out-leakage of fumes into the Dissolver cell. After the sodium nitrate solution has reached its boiling point the steam sparging is discontinued, and 1370 lb. of 50% sodium hydroxide is added from Small Weigh Tank A-2-C at a controlled rate of about 10 lb./min. The heat of the NaOH - Al reaction is sufficient to keep the reacting mixture boiling; the Dissolver Column Condenser returns the water reflux back down the column. Upon completion of sodium hydroxide addition the mixture is further refluxed for about two hours in order to remove the heavy aluminum end-sections of the slug jackets. The charge is then cooled to 40°C. by valving cooling water to the coil, and the coating waste solution is jetted to Waste Holdup Tank H-10.

A 1070-lb. water rinse followed by a 5520-lb. 5% nitric acid rinse is added to the Dissolver, sparged, and finally directed to the Waste Holdup Tank, H-10. The combined coating-removal waste and rinse solutions are jetted from the Waste Holdup Tank to an Underground Storage Tank Cascade.

The exact dissolving schedule for the bare slugs may be dependent upon meteorological conditions in the vicinity of the Plant; the treated and filtered off-gases from the dissolving operation must be adequately diluted by the atmosphere between the time they are discharged from the stack and the time they reach ground level again. If the Redox Dissolver off-gases are more decontaminated from radioiodine than those of the Bismuth Phosphate Plants, a more favorable dissolving schedule (than the night dissolving of the Bismuth Phosphate Plants) may be available for Redox.

Once it has been established that dissolving may begin, about 6370 lb. of 60% nitric acid is charged to the Dissolver from the Large Weigh Tank. During the dissolving period water flow is maintained through the Dissolver Column Condenser to reflux vaporized acid and water, and the Dissolver Vent Jet is operated to produce as high a vacuum as possible in the Dissolver.

Some heating through the Dissolver coil may be required to initiate the dissolution reaction. However, once begun the reaction proceeds quite rapidly, and it may be necessary to use cooling water in order to prevent the vacuum pressure in the vessel from falling below 10 inches of water. As the reaction proceeds it becomes less violent due to consumption and, hence, dilution of the acid, and increased heating is required to maintain the reacting mixture at the boiling point. After a period of about six hours the specific gravity of the boiling solution has reached 1.82 indicating that the acid has been substantially consumed and about one third of the 7700-lb. charge dissolved. Actually the solution still contains about 1% nitric acid. About 1060 lb. (one third) of the batch of previously accumulated slug rinse water is jetted

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from the Rinse Tank to the Dissolver. The addition of the dilution water effectively halts any further nitric acid-uranium reaction and assures the presence of a slight amount of acid in the solution.

After addition of the dilution water to the Dissolver solution at the completion of the cut, the entire mixture is jetted to the Metal Solution Storage Tank, H-9, corresponding to the Dissolver in which the dissolution reaction was carried out.

The second third of the uranium metal charge (second cut) is dissolved in the same manner as the first. The third cut is also identical with the first two except that the time cycle is lengthened from six to about seven hours.

After transferring the third cut to metal solution storage, about 3000 lb. of water is added to the Dissolver to cover the approximately one-ton slug heel that remains. Just before the next charging operation the water is transferred by jet to the Rinse Tank. It is used as dilution water for the three cuts of the next charge.

1.3 Dissolver off-gas treatment

During the dissolution period the nitrogen oxides and volatile fission-product elements evolved, together with air which leaks into Dissolver A-2, pass out through the Dissolver Column vapor line and into the base of the A-3 Off-Gas Heater. The vapors are heated by electrical resistance heaters from an initial temperature of about 80 to 120°F. up to 450 to 500°F. during their travel through the Heater. A temperature controller maintains exit gas temperature between the 450 to 500°F. limits by controlling the rate of heat input to the heating elements. The hot gases pass immediately into a Silver Reactor, A-3, located above the A-3 Heater. During passage through the Reactor, 99.9% of the iodine is removed, and the temperature of the gases falls to about 350°F.(10)

After treatment in the Silver Reactor the iodine-free gases pass through the Fiberglas Filter, A-4, for removal of particulate matter and thence to the Stack for discharge into the atmosphere. The driving force directing passage of the off-gases from the Dissolver through the Heater, Silver Reactor, and Fiberglas Filter is supplied by the Dissolver Vent Jet, located near the Stack.

During the coating-removal operation the off-gas consists principally of air which leaks into the Dissolver plus small amounts of ammonia and hydrogen evolved by the reaction. It may be necessary to by-pass (by means of the remote valving provided) the Fiberglas Filter to prevent the small quantities of ammonia from reacting with moisture and oxides of nitrogen that may reside in the Filter is small amounts. Formation of ammonium nitrate might increase Filter pressure drop excessively. Tests are under way to establish whether or not by-passing the Filter during coating removal is a necessity.

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It is possible that an Off-Gas Scrubber will be utilized at a later date for removal of nitrogen oxides from Dissolver off-gases. In scrubbing, the gases rising through the Scrubber Column are contacted by a solution (nearly saturated in $NaNO_2$ and $NaNO_3$ and containing about 6% free NaOH) which flows down through the Raschig-ring column packing. Part of the solution falling through the column is fresh 40% NaOH fed continously during the scrubbing period from an Off-Gas Scrubber Caustic Tank at the rate of about 2.7 gal./min. Recirculating $NaNO_2$-$NaNO_3$ solution (composition due to nitrogen oxides absorption in caustic) in amount equal to about 5 to 6 times the volume of fresh caustic is returned to the top of the column by pump. Remote valving in the pump discharge line diverts a portion of this solution to an Underground Storage Cascade.

1.4 Metal solution storage

By referring to Figure III-3 it may be seen that three Metal Solution Storage Tanks with a total capacity of several days' supply of uranium solution (actually about 10,000 gal.) are provided for the Redox Plant. Storage Tank H-9 receives from Dissolver A-2-A; H-8, from Dissolver A-2-B; and either H-9 or H-8, from spare Dissolver A-2-C. Since all three cuts of a particular dissolving charge must be collected in the same storage tank there is a blending of the cuts which tends to produce uniformity of composition. Uniformity of composition between charges is attained in some degree by the necessity of routing the contents of Tanks H-9 and H-8 to a large storage tank, H-7 (TK-108).

1.5 Oxidation and scavenging

A daily charge of uranium solution is transferred by jet from Metal Solution Storage Tank H-7 to Oxidizer H-4. The daily instantaneous processing rate of 3-1/8 tons of uranium per day corresponds to about 1600 gal. of solution in the Oxidizer.

Several alternative procedures are available for the oxidation-scavenging operations. They are briefly summarized as follows:

1.51 $KMnO_4$ procedure with MnO_2 scavenging

The uranium solution in the Oxidizer, H-4, is made 0.03 M in potassium permanganate ($KMnO_4$), 0.09 M in sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$), and heated to about 95°C. by means of coil steam. Negative pressure is maintained in the vapor space of the Oxidizer and in the Oxidizer Column, E-4, by the Oxidizer Vent Jet. After reaching operating temperature the solution is sparged with air for four hours at the rate of about 200 cu.ft./min. The air serves as a carrier gas to sweep out the volatile ruthenium tetroxide (RuO_4) formed by the oxidizing action of the $KMnO_4$. At the end of the four-hour ruthenium distillation period, one mole of chromic nitrate per mole of $KMnO_4$ not yet reduced plus 5% excess chromic nitrate, based on the original amount of $KMnO_4$ present, is added to the hot solution in the Oxidizer. The MnO_2 precipitate is digested for about one-half hour at 75°C. to aid in the adsorption of zirconium and niobium. The Oxidizer slurry is jetted to the rotating Centrifuge bowl at the rate of about 2 gal./min. The Centrifuge, H-2, should be

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operated at its maximum speed of 1740 rev./min. (1730 G). The supernate liquor overflows into the IAF Make-Up Tank, H-1. After approximately half of the Oxidizer slurry has been jetted to the Centrifuge the cake volume is about 20 gal. Feed to the Centrifuge is discontinued and about 40 gal. of supernate, held up in the 60-gal. bowl, is skimmed to the IAF Make-Up Tank. The cake is washed about four times with 40 gal. of 0.01 M HNO_3 solution each time and washes are skimmed to the Oxidizer via the jet in the Centrifuge effluent line. The cake is dissolved by the addition, through the bowl sprays to the slowly rotating Centrifuge bowl, of about 40 gal. of solution consisting of about 20% ferrous sulfamate and 10% nitric acid. The dissolved cake solution is jetted to the Slurry Hold-Up Tank, H-3. The remaining portion of Oxidizer slurry is then routed through the Centrifuge, the supernate is skimmed, and the cake is washed and dissolved in an identical manner to that described for the first half of the batch. It may be noted that this procedure corresponds to that listed in Figures III-2 and III-3.

1.52 $KMnO_4$ procedure without scavenging

The uranium solution in the Oxidizer, H-4, is made about 0.03 M in potassium permanganate, 0.09 M in sodium dichromate, and heated to about 95°C. by means of coil steam. As before, negative pressure is maintained in the vessel. After reaching operating temperature the solution is sparged with air for about four hours at the rate of about 200 cu.ft./min. About 20 to 50% excess of chromic nitrate is added at the conclusion of the sparge period to reduce all manganese ions to the soluble manganous nitrate. (See Subsection D4.) The solution is jetted at approximately 2 gal./min. to the rotating Centrifuge bowl where gross particles are removed. After the Oxidizer has been emptied, the supernate held up in the Centrifuge bowl is skimmed foward to the IAF Make-Up Tank. Periodically it will be necessary to remove the gross particles accumulated in the Centrifuge bowl. This may be accomplished by slurry-out methods or by dissolution of the particles.

1.53 Ozone-Filtrol procedure

The uranium solution in the Oxidizer, H-4, is made about 0.01 M in potassium permanganate and heated to about 95°C. by means of coil steam. Negative pressure is maintained in the vapor space of the Oxidizer and in the Oxidizer Column, E-4, by the Oxidizer Vent Jet. After reaching operating temperature the solution is sparged for about six hours at the rate of about 200 cu.ft./min. with a gas consisting of 2% ozone in air. The ozone oxidizes and sweeps RuO_4 out of solution. At the end of the ruthenium distillation period the solution is made about 0.1 M in $Na_2Cr_2O_7 \cdot 2H_2O$. Following dichromate addition all the manganese is reduced to soluble manganous nitrate by the addition of an excess of chromic nitrate. About 220 lb. of Super Filtrol F.O. is added in slurry form to the Oxidizer and digested at 95°C. for one-half hour. The slurry is jetted to the rotating Centrifuge bowl at the rate of about 3 gal./min. After about one half of the batch has been centrifuged, supernate skimming and cake-washing methods as described under G1.51, above, are carried out, and the Super Filtrol cake is slurried to the Slurry Hold-Up Tank, H-3. The remaining half of the Oxidizer

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batch is then processed in like manner. After sampling of the Filtrol cake in the Slurry Hold-Up Tank shows tolerable plutonium losses (less than 0.1%) the slurry is jetted to an Underground Storage Cascade. Upon completion of slurry jetting, the line to the Cascade is flushed with about 500 gal. of water.

Because of the reasons discussed in Subsection C3.3 the plant Ozonizer may not actually be installed.

1.54 Modified procedures

The three specific procedures suggested above may have several variations. The sparge gas for any of the procedures might be air, ozone, or steam. If steam were used, operating temperature for the ruthenium distillation operation would be the boiling temperature of the solution.

In the event of too rapid $KMnO_4$ decomposition in the Oxidizer, an incremental addition of $KMnO_4$ may be indicated for either of the two $KMnO_4$ procedures. A procedure used in semiworks studies makes the dissolver solution 0.01 M in $KMnO_4$ initially. A second equal portion of $KMnO_4$ is added to the solution after 1-1/2 hours of sparging, and a third portion after 3 hours. If the uranium solution is made 0.08 M in $KMnO_4$ initially, semiworks data indicate that a sufficient fraction of $KMnO_4$ remains undecomposed at the end of the ruthenium volatilization step, but the larger quantity of MnO_2 formed lengthens the centrifugation cycle.

Other satisfactory reducing agents for MnO_2 cake dissolution (H_2O_2 or $Cr(NO_3)_3$, for example) may be substituted for Fe(II) in Subsection 1.51.

Although the Oxidizer Column is equipped with a reflux condenser the condenser is not normally used for any of the procedures because of the probability of refluxing some of the RuO_4 back to the Oxidizer. Replacement water (for that lost in the non-refluxed vapors) is added as required from Chemical Addition Tank H-4-C- in order to prevent freezing of the contents of the Oxidizer if cooling of the solution is required.

1.6 Ruthenium scrubbing

The volatilized RuO_4, water vapor, and carrier gas are directed into the Ruthenium Scrubber, H-5. In the Scrubber the hot gases are contacted countercurrently with 25% sodium hydroxide, and the RuO_4 is removed almost quantitatively as sodium ruthenate. The caustic scrub is batch-charged to the Ruthenium Scrubber and during Scrubber operation is continuously recycled from the Scrubber pot to the distributor near the top of the packed section. A short packed deentrainment section above the distributor minimizes entrained liquid that would otherwise carry over with the scrubbed gases. The Scrubber is operated at approximately the same temperature as the Oxidizer to avoid excessive caustic dilution due to condensation in the Scrubber of large amounts

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of water vapor. Periodically, on the order of twice a week, the caustic solution in the Scrubber is jetted to the Waste Neutralizer (see Chapter X) and replacement is made with fresh 25% sodium hydroxide.

The exit gases from the Scrubber, still containing large amounts of water vapor, are passed through a condenser to remove the water. The Oxidizer Vent Jet, providing the driving force for the vapors, draws the residual, relatively dry gases through a Fiberglas capsule for removal of remaining particulate matter and thence discharges them to the Stack.

1.7 IAF adjustment

The daily batch of solution, oxidized and centrifuged, consists of about 1370 gal. About 800 lb. of 25% sodium hydroxide solution is added to the uranium solution in the IAF Make-Up Tank, H-1. Dilution of the solution to about 1580 gal. is then accomplished by the addition of about 900 lb. of water. Water and 25% sodium hydroxide are both added from Chemical Addition Tank numbered "H-1 and 3-A". Uniformity of composition in the IAF Make-Up Tank is attained by agitation.

When the volume remaining in IA Feed Tank F-7 is small enough to permit the transfer of the contents of the IAF Make-Up Tank, a submerged pump effects the move at a rate of about 50 gal./min. in about 0.5 hour.

2. Remedy of Off-Standard Conditions

2.1 Excessive fission-product activity in Stack

The condition whereby too high a proportion of ruthenium tetroxide escapes from the Ruthenium Scrubber can be corrected in some degree by increasing the caustic recirculation rate in the Scrubbers. An alternative or concomitant method is to reduce the gas flow rate to the Scrubbers. This, however may require lengthening the time of the ruthenium distillation operation. If too much iodine escapes from the Silver Reactor, the unit will probably require replacement.

Detection of either of the conditions mentioned above would be made by Stack sampling methods described in Chapters X and XXI.

2.2 Greater than normal Ru, Nb, or Zr activity in IAF

This problem may be handled in two ways. The feed may be sent ahead to the Extraction Battery and either an additional decontamination cycle may be employed, or rework of one or both of the product streams may be undertaken if decontamination specifications are not satisfied. Alternatively, the feed may be returned to the Oxidizer for additional treatment (ruthenium distillation and scavenging) in that vessel.

This off-standard condition may be detected from samples taken at numerous points in the process or from the inability to meet fission-product specifications in the product streams.

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2.3 Carry-over of fines from centrifugation

The solution may be sent ahead with recognition that the solvent-extraction columns may have to be cleaned out earlier than would otherwise be necessary. (However, pilot-plant column operation indicates that fines, especially MnO_2 fines, are swept out in the IA Column aqueous waste). A second alternative is to return the solution to the Oxidizer for refeeding to the Centrifuge.

This condition may be detected from samples or, if especially bad, by reduced quantity of cake (measured by weight factor after cake dissolution) over that expected. It might not be detected until column performance is affected.

2.4 Excessive U or Pu loss with filter cake

Excessive losses of uranium or plutonium (greater than 0.1%) with the filter cake slurry or solution may be recovered by recycling the material from the Slurry Holdup Tank to the Oxidizer. The small quantity of solution or slurry would normally be processed with the next Oxidizer batch.

This condition is detected by routine accountability samples of the cake slurry or solution.

2.5 Formation of plutonium (IV) polymer

Plutonium (IV) polymer formation might result from inadvertent dissolving to acid deficiency or from a possible reduction from Pu(VI) in the presence of an acid-deficient solution in the IAF Make-Up Tank. In either event, since only strenuous hot oxidation methods, e.g., treatment for 2 to 6 hours with 0.1 M sodium dichromate near boiling temperature, seem adequate for converting Pu (IV) polymer to Pu (VI), the solutions would have to be routed to the Oxidizer, the only vessel capable of giving the required treatment.

The condition might be detected from samples indicating excessive plutonium losses in the IA Column.

2.6 Necessity of rapidly arresting uranium dissolution reaction

If dissolving proceeds too rapidly, positive pressure may be built up in the Dissolver. Coil cooling water may be used to reduce the rate of reaction. In cases of extreme emergency, the water in the Dissolver Drowning Tank may be dropped into the Dissolver very rapidly, thus almost immediately arresting the reaction. Excessive pressure in the Dissolver will be indicated by pressure recorders over the Dissolver Column.

2.7 Sludge build-up in the Dissolver

Incomplete removal of solids (bonding material and scale sludges) may be expected when jetting solutions out of the Dissolver. If the high silicon-content sludge contributes more foreign material than can be removed in centrifugation or if the tendency toward solution emulsi-

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fication is increased to the extent that column operation is impaired, then the need for sludge removal from the Dissolver may be indicated. A convenient method for sludge dissolution is by use of a solution of 5% HF in 10% HNO_3. Because of the corrosive effect of this solution on the Dissolver, solution contact time with the Dissolver should be kept to a minimum; about 10 minutes at 100°C. should be adequate for removing most of the sludge. A 30% HNO_3 passivation flush should follow the HF treatment.

This off-standard condition might be detected through erratic interface instrument action on the IA Column or increase in silicon as determined by spectroscopic assay on uranium or plutonium product streams.

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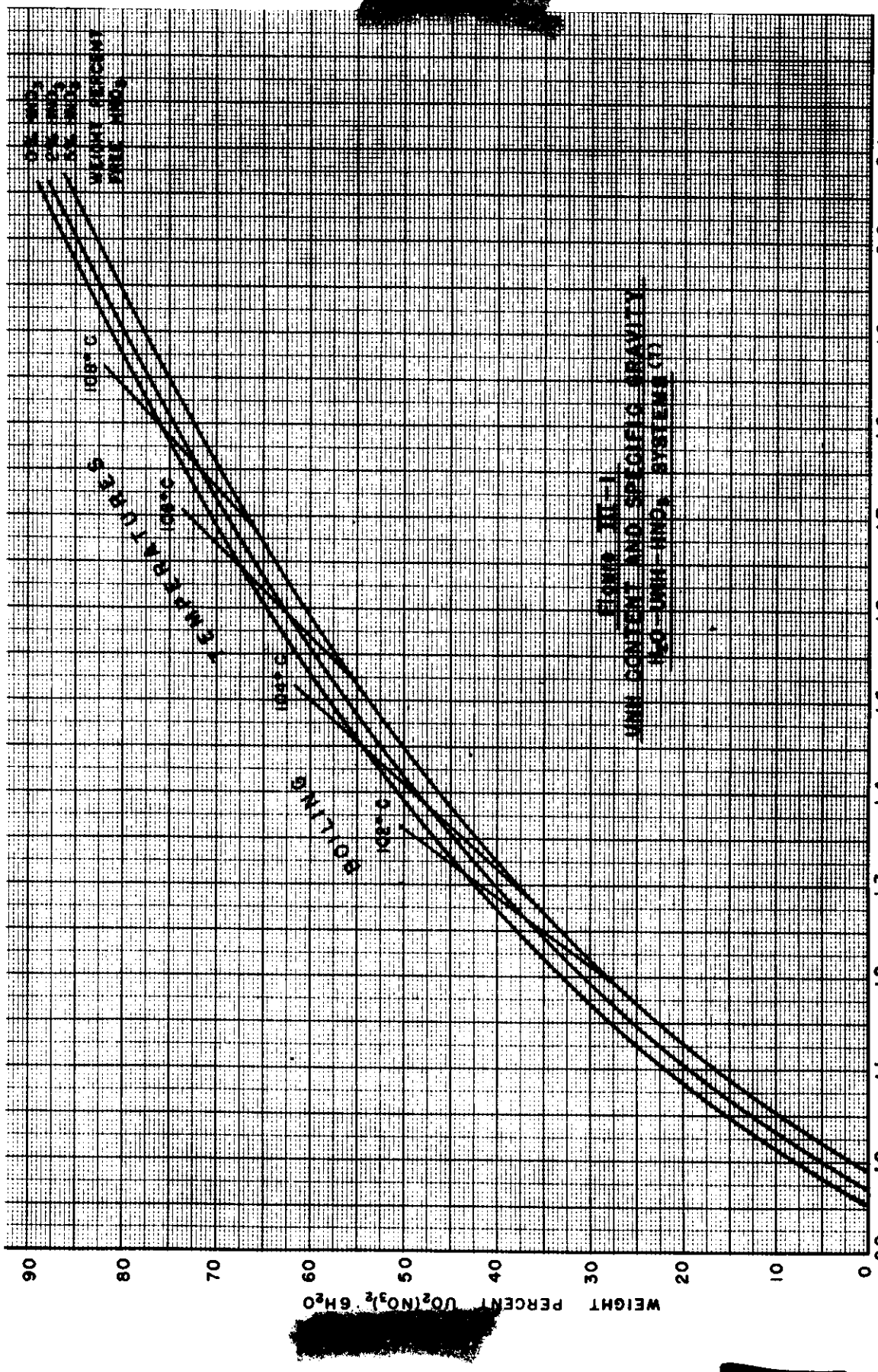

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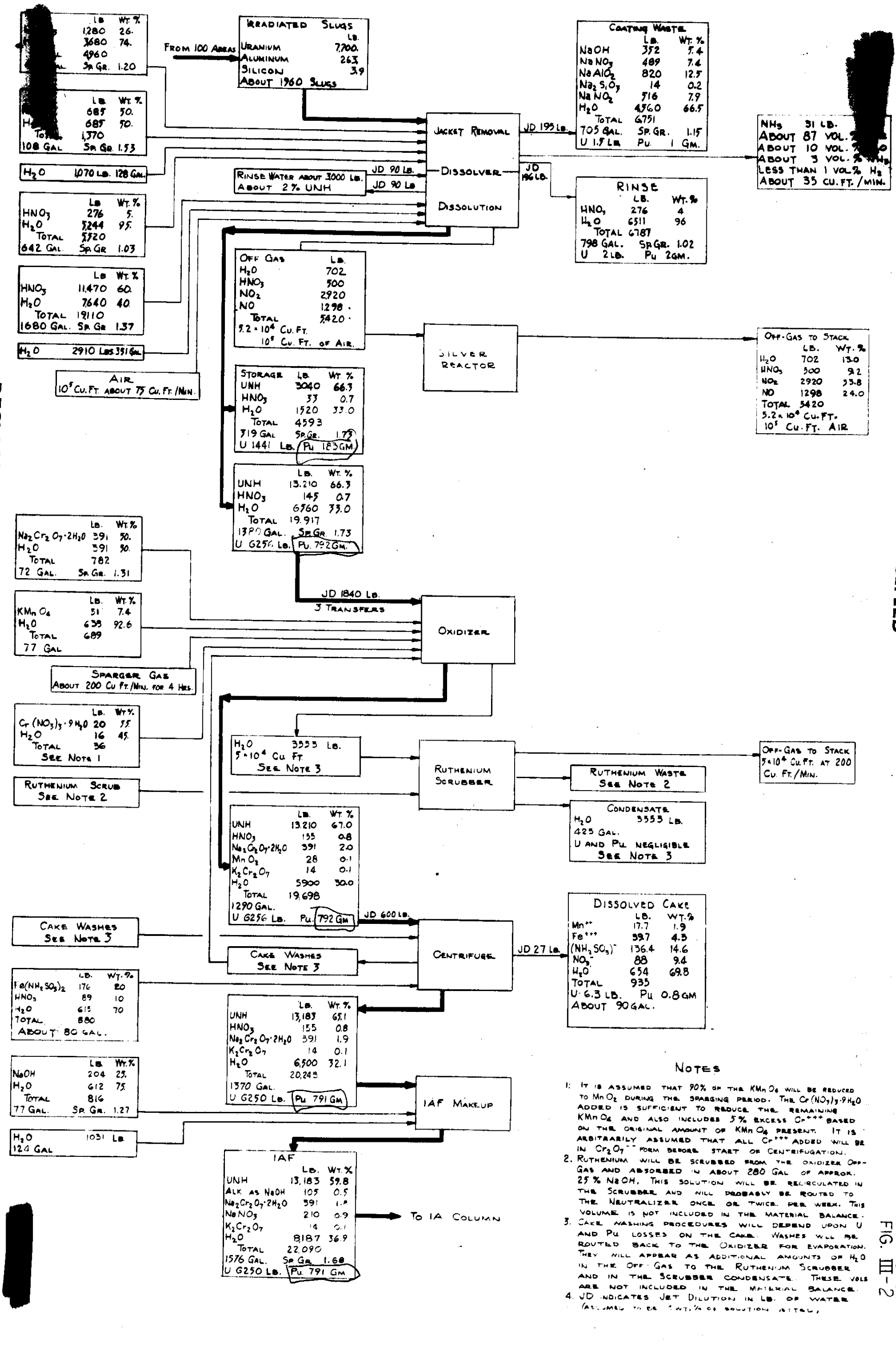
FIGURE III-2

MATERIAL BALANCE FLOWSHEET – URANIUM FEED PREPARATION

Based Upon SK-2-5351 Sheet 1

BASIS: PROCESSING OF 6250 LB. OF U PER DAY (DESIGN INSTANTANEOUS RATE), EXCEPT THAT DISSOLVER DATA ARE BASED UPON A NORMAL 7,700 LB. U CHARGE.



NOTES

1. IT IS ASSUMED THAT 90% OF THE $KMnO_4$ WILL BE REDUCED TO MnO_2 DURING THE SPARGING PERIOD. THE $Cr(NO_3)_3 \cdot 9H_2O$ ADDED IS SUFFICIENT TO REDUCE THE REMAINING $KMnO_4$ AND ALSO INCLUDES 5% EXCESS Cr^{+++} BASED ON THE ORIGINAL AMOUNT OF $KMnO_4$ PRESENT. IT IS ARBITRARILY ASSUMED THAT ALL Cr^{+++} ADDED WILL BE IN $Cr_2O_7^{--}$ FORM BEFORE START OF CENTRIFUGATION.
2. RUTHENIUM WILL BE SCRUBBED FROM THE OXIDIZER OFF-GAS AND ABSORBED IN ABOUT 280 GAL OF APPROX. 25% NaOH. THIS SOLUTION WILL BE RECIRCULATED IN THE SCRUBBER AND WILL PROBABLY BE ROUTED TO THE NEUTRALIZER ONCE OR TWICE PER WEEK. THIS VOLUME IS NOT INCLUDED IN THE MATERIAL BALANCE.
3. CAKE WASHING PROCEDURES WILL DEPEND UPON U AND Pu LOSSES ON THE CAKE. WASHES WILL BE ROUTED BACK TO THE OXIDIZER FOR EVAPORATION. THEY WILL APPEAR AS ADDITIONAL AMOUNTS OF H_2O IN THE OFF-GAS TO THE RUTHENIUM SCRUBBER AND IN THE SCRUBBER CONDENSATE. THESE VOLS ARE NOT INCLUDED IN THE MATERIAL BALANCE.
4. JD INDICATES JET DILUTION IN LB. OF WATER (ASSUMED TO BE 1 WT.% OF SOLUTION JETTED)

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FIG. III-2

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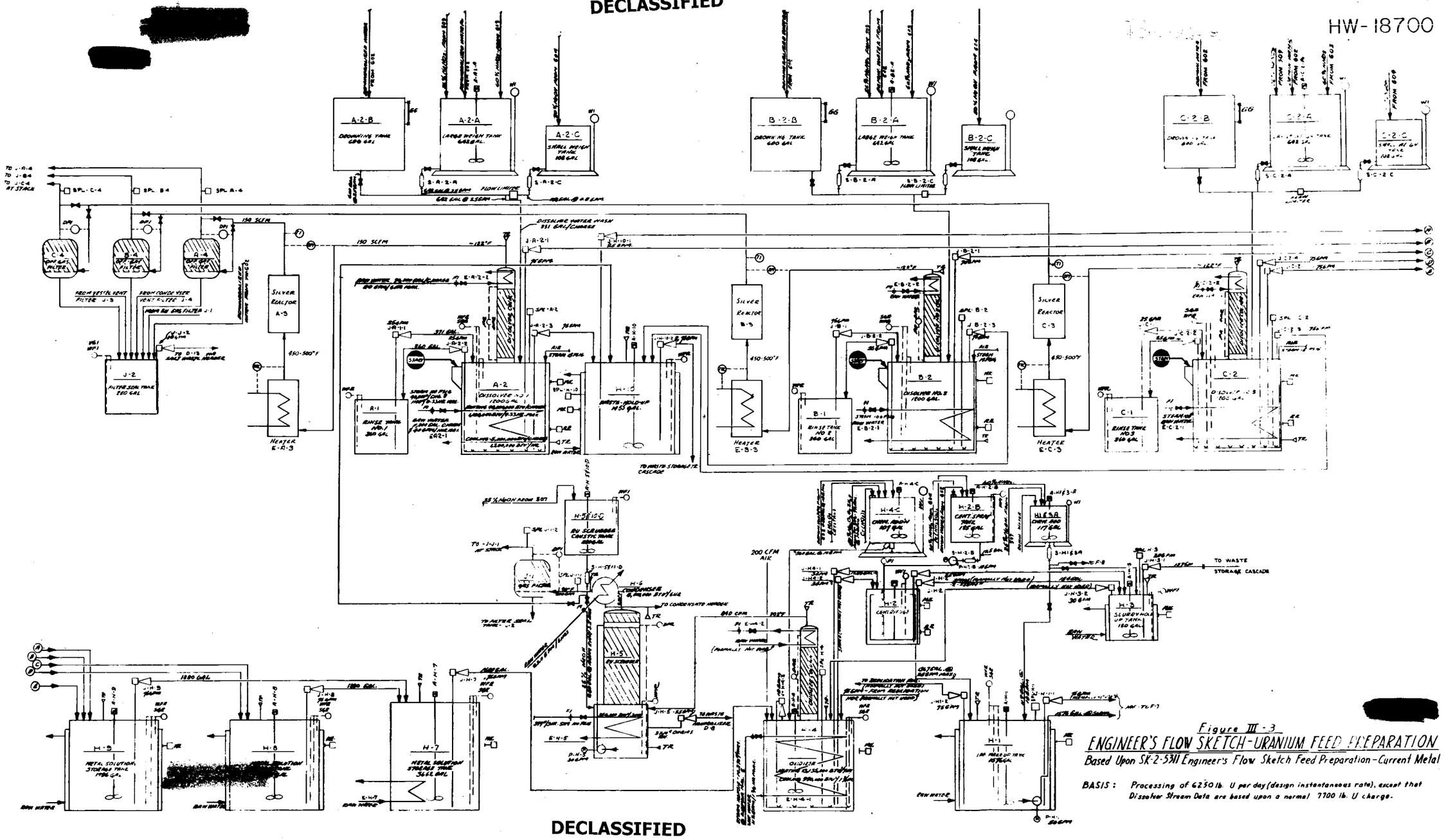

Figure III-3

ENGINEER'S FLOW SKETCH-URANIUM FEED PREPARATION

Based Upon SK-2-5311 Engineer's Flow Sketch Feed Preparation-Current Metal

BASIS: Processing of 62501b. U per day (design instantaneous rate), except that Dissolver Stream Data are based upon a normal 7700 lb. U charge.

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PART II. PROCESS, continued

CHAPTER IV. PROCESS CHEMISTRY (SOLVENT-EXTRACTION)

CONTENTS

		Page
A.	PROCESS DESCRIPTION	403
1.	Basic Principles	403
1.1	Introduction	403
1.2	Solute distribution between equilibrated liquid phases	403
1.3	Introduction to solvent-extraction	411
1.4	Determination of phase-equilibrium data	412
1.5	Solvent-extraction effectiveness	413
1.6	Chemical bases of the Redox process flowsheets	414
2.	IA Column	416
3.	IB Column	422
4.	IC Column	427
5.	ICU Concentration	429
6.	2D Column	430
7.	2E Column	432
8.	Third Uranium Decontamination Cycle	433
9.	Cross-Over Oxidation	434
9.1	General principles	434
9.2	Dichromate oxidation	435
9.3	Other oxidants	437
10.	2A Column	438
11.	2B Column	440
12.	Third Plutonium Decontamination Cycle	440
B.	PROPERTIES OF PROCESS MATERIALS	441
1.	Hexone	441
2.	Hexone-Water	443
3.	Other Solutions in Hexone	444
4.	Aqueous Aluminum Nitrate Solutions	448
5.	Aqueous Uranium Nitrate Solutions	451
6.	Aqueous Plutonium Nitrate Solutions	454
7.	Sulfamic Acid	460
8.	Ferrous Sulfamate	462
9.	Interfacial Tension and Phase Disengaging Times	464
10.	Heats of Extraction	466
C.	HEXONE-AQUEOUS PHASE EQUILIBRIA	468
1.	Uranium	468
1.1	Introduction	468
1.2	Distribution ratio in salted (IA-type) systems	468
1.3	IA Column equilibrium diagrams	469
1.4	Distribution ratio in unsalted (IC-type) systems	469
1.5	IC Column equilibrium diagram	470

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CONTENTS

		Page
2.	Plutonium	470
2.1	Introduction	470
2.2	Plutonium (VI) distribution	470
2.3	Plutonium (V) distribution	472
2.4	Plutonium (IV) distribution	473
2.5	Plutonium (III) distribution	474
2.6	Equilibrium lines	475
3.	Neptunium	476
4.	Fission Products	478
4.1	Introduction	478
4.2	Gross beta	478
4.3	Gross gamma	478
4.4	Ruthenium	479
4.5	Zirconium and niobium	480
4.6	Cerium	483
4.7	Other fission products	485
4.8	Fission-product distribution ratios vs. decontamination performance	486
5.	Nitric Acid	487
6.	Others	490
6.1	Sulfamic Acid	491
6.2	Ferrous sulfamate	491
6.3	Chromium	491
6.4	Iron	491
6.5	Aluminum	492
6.6	Sodium	492
REFERENCES		492
		493

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CHAPTER IV. PROCESS CHEMISTRY (SOLVENT-EXTRACTION)

A. PROCESS DESCRIPTION

1. Basic Principles

1.1 Introduction

The Redox process utilizes solvent-extraction to recover uranium and plutonium from irradiated uranium slugs. In the process the uranium and plutonium are recovered as separate aqueous solutions of their nitrates, which are relatively free from other transuranium as well as fission-product elements formed during irradiation of the slugs. The composition of the irradiated slugs is given in Chapter II, while the preparation of Redox feed solution from the slugs is described in Chapter III. Chapter IV embodies a discussion of the chemistry of the solvent-extraction system from the prepared feed solution to the separate, concentrated, uranium and plutonium product streams.

The information contained in Chapter IV is divided into three parts: Section A is a discussion of the chemical variables of the process, Section B contains a detailed data summary of the physical and chemical properties of the process materials, and Section C gives a detailed summary of the equilibrium data for the mass transfer of Redox process components between aqueous and hexone phases. Subsection 1 of Section A is a discussion of the basic physical chemical principles of solvent-extraction leading to the formulation of alternative Redox chemical flowsheets; the remaining subsections discuss in greater detail the application of the basic principles to the individual steps of the Redox process flowsheets.

1.2 Solute distribution between equilibrated liquid phases

If an aqueous solution of uranyl nitrate is placed in a beaker and a layer of hexone is added, it quickly becomes apparent that some of the uranyl nitrate solute in the aqueous phase transfers to the organic solvent. The operation is referred to as solvent-extraction and the mass transfer may be followed qualitatively by observation of the change in color of the two liquid phases, or quantitatively by analysis of the separate phases. Similarly, if the hexone layer is removed from the above system and placed in contact with fresh water, some of the uranyl nitrate solute transfers back to the aqueous phase. The latter mass transfer operation is referred to as stripping to indicate the removal of a desired solute such as uranyl nitrate from a solvent phase such as hexone.

If either of the above two-phase systems is agitated to cause intimate intermixing of the two immiscible liquid phases, it is found that the uranyl nitrate concentration in each phase becomes constant, although usually not the same concentration in both phases. When constant concentrations have been attained, a dynamic equilibrium has become established with the number of uranyl nitrate molecules leaving the aqueous phase equal to the number returning in a given time. This process of attaining equilibrium between the two phases is termed "equilibration" of.

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the phases. It has been found experimentally that the distribution of a solute in such a two-phase system depends on the relative solubility of the solute in each phase. The distribution of uranyl nitrate may therefore be altered by the simple expedient of altering the relative solutility of the uranyl nitrate in either the aqueous or the hexone phase.

The system is directly comparable to the equilibrium between a confined gas and a solution of the gas. Thus if carbon dioxide is confined with some water, the CO_2 becomes distributed between the gaseous phase and the aqueous solution. If the solubility of the carbon dioxide in the water is reduced, as by the addition of ordinary salt to the water, the equilibrium is temporarily upset, releasing some of the dissolved gas and resulting in a higher distribution of the CO_2 to the gaseous phase. On the other hand, if what might be called a CO_2-complexing agent, such as ammonia, is added to the water, the solubility of the carbon dioxide in the aqueous phase is increased. Then the equilibrium distribution of the CO_2 is shifted in favor of the aqueous phase.

In the Redox solvent-extraction system the relative solubilities of the nitrates of uranium, plutonium, and the fission-product elements are similarly controlled in order to effect their separation from each other. The factors affecting relative solubility and therefore the distribution ratio between water and an organic solvent include the nature of the solvent, solvation, temperature, salting in the aqueous phase, hydrogen ion concentration, the state of oxidation of the various cations, and complex formation. These factors are discussed under 1.21 through 1.27, below.

1.21 Distribution ratio

The ratio between the concentrations of a given solute (e.g., uranyl nitrate) in each of two liquid phases in contact equilibrium is variously referred to as the distribution ratio, distribution coefficient, or partition coefficient. It is designated by the letter E to which a subscript and superscript are appended to indicate which phase is the reference phase. Thus for uranyl nitrate, E_a^o (or E_a^h) indicates the ratio of the concentration of the uranyl nitrate in the organic (or hexone) phase to the concentration in the aqueous phase. The numerical value of a given distribution ratio will vary according to whether the concentrations are expressed on a weight basis (such as grams of uranyl nitrate per gram of solution), or on a volume basis (such as grams of uranyl nitrate per liter of solution). However, the volume basis is used throughout this manual unless otherwise indicated.

It is to be noted that, for a given system at equilibrium, the solute concentration ratio may be expressed in two ways, and the basis being used should always be clearly stated and understood. Thus the distribution ratios:

$$E_a^o = 4.0$$

and

$$E_o^a = 0.25$$

may both be used to identify the same mass transfer equilibrium in which the uranyl nitrate concentrations are 20 g./l. in the hexone phase and 5.0 g./l. in the aqueous phase.

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The distribution of uranyl nitrate tends to be relatively constant at low concentrations (ca. 10 g./l. in the aqueous phase) in hexone-aqueous systems, but it varies markedly at higher concentrations as may be seen by reference to Figure IV-31. By way of comparison with another system, uranyl nitrate distribution appears to be largely independent of concentration in aqueous-dibutyl cellosolve phase equilibrium (an alternative uranium solvent-extraction system).

The distribution ratio is the ratio of the solute concentrations regardless of the relative volumes of the two liquid phases. It is apparent, however, that the amount of uranyl nitrate extracted from aqueous solution by hexone, for example, is dependent upon the relative volume of hexone used as well as the uranyl nitrate distribution ratio. The mass transfer relationship between the distribution ratio and the phase volume ratio is expressed by the extraction factor, which is discussed briefly in 1.52, below, and more extensively in Chapter V.

1.22 Choice of solvent

For the separation of uranium, plutonium, and fission products by solvent-extraction, the choice of the solvent to be used depends upon an optimum combination of the following solvent characteristics: (a) extraction effectiveness and selectivity for uranium and plutonium, (b) low mutual solubility with an aqueous phase in contact, (c) chemical stability in the system, (d) low vapor pressure and high flash point, (e) suitable density, viscosity, and interfacial tension in the system, (f) ease of purification for recovery by such methods as distillation, (g) availability and low cost, (h) non-corrosiveness, and (i) low toxicity. Early in the development work on a solvent-extraction separation process, hexone was found to meet the decontamination, availability, and recovery requirements fairly well. Therefore, while the search for better solvents was still in progress, the hexone (Redox) system was developed into a workable process in spite of the fact that it was recognized that more suitable solvents might be developed later. For the properties of hexone reference is made to Subsections B1, B2, and B3.

1.23 Solvation

Solvation refers to the binding of solvent molecules to dissolved solute ions or molecules by physical or chemical forces. In the uranyl nitrate-water-hexone system in the beaker experiment mentioned previously, the uranyl nitrate is hydrated in the aqueous phase. When the uranyl nitrate transfers to the hexone solvent, the mass transfer occurs as molecules of uranyl nitrate associated with three to four molecules of water. In the organic phase the uranyl nitrate is solvated with probably two molecules of hexone in addition to the water which participated in the transfer (see Subsection B3).

Alteration of the state of solvation of a solute in one phase of a two-phase system alters the relative solubilities of that component in the two phases. Thus if aqueous uranyl nitrate solution is added to a beaker containing a hexone solution of nitric acid, ruthenium$^{(133)}$, or cerium$^{(111)}$ the latter components may be at least partly displaced from the organic

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to the aqueous phase. The distribution ratio of the displaced component is thereby altered. In the competition of the solute molecules for solvation by hexone, the uranyl nitrate forms the stronger solvation bonds with the hexone and therefore displaces the fission products or acid from hexone solvation complexes. The situation is comparable to the top of the Redox IA Column extraction section where concentrated aqueous uranyl nitrate solution is meeting a hexone stream which has been equilibrated with the aqueous fission product waste stream. The resulting effect of displacing fission-products from hexone solution back to the aqueous phase is sometimes referred to as "back salting".

1.24 Salting

A common method of reducing the solubility of a compound in a given solution is by the "salting" effect of a common ion. Thus the addition of a nitrate to an aqueous solution of uranyl nitrate will reduce the uranyl nitrate solubility in the solution. If such an aqueous solution is in contact equilibrium with a hexone phase, the solubility of the uranium in the aqueous phase is decreased relative to the hexone phase. The E_a^h distribution ratio is thereby increased.

The uranyl nitrate is largely ionized in the aqueous phase, but it is transferred in the molecular state into the hexone. Then the effect of salting on mass transfer equilibrium can be explained by reference to the mass-action law relationship expressed in the following equation:

$$[UO_2^{++}]_{AQ.} + 2[NO_3^-]_{Aq.} + xH_2O \rightleftharpoons [UO_2(NO_3)_2 \cdot xH_2O]_{Aq.} \rightleftharpoons [UO_2(NO_3)_2 \cdot xH_2O]_{Org.}$$

The addition of nitrate ion to the aqueous phase decreases the ionization of the aqueous uranyl nitrate and increases the transfer of the molecular salt to the organic phase.

The same effect is produced by simply increasing the concentration of the uranyl nitrate in the aqueous phase. However, it takes a large increase in $UO_2(NO_3)_2$ concentration to decrease the ionization of the salt materially, as may be seen by reference to the following table:(6)

Ionization of Uranyl Nitrate

Aqueous $UO_2(NO_3)_2 \cdot 6H_2O$ molarity	2.0	1.0	0.5	0.25	0.125
Grams $UO_2(NO_3)_2 \cdot 6H_2O$ per liter	1004	502	251	125.5	62.75
Degree of ionization	0.78	0.80	0.82	0.88	0.94

Therefore an increase in aqueous $UO_2(NO_3)_2$ concentration from 0.5 to 1.0 M, for example, will result in the presence in the hexone phase of a lower proportion of the total uranyl nitrate in the two-phase system.

The extent of the salting action produced by a given agent is not only dependent upon the amount of common ion added but also on the solvation of the cation of the added salt.(42,127,128) Thus one equivalent of aluminum nitrate will have greater salting effect than an equivalent of sodium nitrate partly because of the hydration of the aluminum ion as compared with the sodium ion. Withdrawal of aqueous solvent by the

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hydration of the added cation has the effect of increasing the nitrate concentration and producing added salting.

Differences in the salting effects of different electrolytes are also dependent upon the ionic strengths of the compounds.(4) The ionic strength, μ, is a concentration property which takes into account the effect of interionic attraction by including the ionic charges. It is defined by the equation:

$$\mu = \frac{(m_+)(e_+)^2 + (m_-)(e_-)^2}{2}$$

where m_+ and m_- are the respective molalities (gram-moles per thousand grams of solvent), and e_+ and e_- are the respective charges or valences of the positive and negative ions. For comparison of the salting effect of sodium nitrate with aluminum nitrate, the ionic strength of a 0.1 molal sodium nitrate solution is:

$$\mu = \frac{(0.1)(1)^2 + (0.1)(1)^2}{2} = 0.1$$

For 0.1 molal aluminum nitrate the ionic strength is:

$$\mu = \frac{(0.1)(3)^2 + (0.3)(1)^2}{2} = 0.6$$

Therefore, one mole of hydrated aluminum nitrate (375 g.) has six times the ionic strength of a mole of sodium nitrate (85 g.) dissolved in the same quantity of solvent, or 0.735 gram of $Al(NO_3)_3 \cdot 9H_2O$ is equivalent in salting strength to one gram of sodium nitrate. The relationship is used in the salting strength calculations described in Chapter V.

The choice of a salting agent for the Redox process was dependent upon the following factors: (a) availability, cost, and possibility of recovery, (b) chemical stability and inertness toward the system, (c) effect on volumes and neutralization requirements of the waste solutions, (d) insolubility in hexone, (e) effectiveness in producing high distribution ratios at low degrees of saturation, (f) selectivity in salting the desirable components of the system (decontamination), and (g) the effect on interfacial tension, aqueous density, and viscosity in the system.

Ammonium nitrate and aluminum nitrate have been extensively tested in the Redox system, and a number of other salts have been tried. See Figure IV-30 for a comparison of the effects of ammonium nitrate, calcium nitrate and aluminum nitrate on the distribution of uranium into hexone. Aluminum nitrate was chosen for the Redox process largely on the basis of its stability in addition to its general conformity with the other requirements.

1.25 Temperature

If heating or cooling is applied to an aqueous-hexone system which has been equilibrated in a beaker, a change is produced in the distribution of a component dissolved in the two-phase system. This change in the distribution ratio may be due to two factors. The temperature coefficient of solubility of Redox process components is different for aqueous and hexone solutions, and consequently a temperature change produces a change in the relative solubilities of a given component in the two phases. Furthermore, the transfer of a solute from water to hexone solution may involve a heat exchange due to the formation and separation of hydration and solvation bonds as in the case of uranyl nitrate.

The following equation may be used to express the equilibrium for the transfer of uranyl nitrate between aqueous and hexone phases:

$$[\,UO_2(NO_3)_2 \cdot 6H_2O\,]_{Aq.} \rightleftharpoons [\,UO_2(NO_3)_2 \cdot xH_2O\,]_{Hex.} + (6 - x)H_2O + \text{Heat.}$$

In other words when hexone is added to an aqueous solution of uranyl nitrate in a beaker, heat is evolved by the transfer of some of the uranyl nitrate to the hexone phase. Then if the temperature is raised after allowing the system to come to equilibrium, by application of the principle of Le Chatelier to the above equation it may be seen that some of the uranyl nitrate is transferred back to the aqueous phase. The effect is illustrated by the following table of coefficients showing decreased distribution into the organic phase as the temperature is raised.(44)

Variation of Uranyl Nitrate Distribution

With Temperature

Temperature, °C.	E_a^o
11	255
15	191
21	151
27	121
35	84.1

Aqueous phase: 0.12 M $UO_2(NO_3)_2$;

2.4 M $Al(NO_3)_3$.

The heat effect illustrated in the above equation is apparent in the Redox process by the evolution of heat in the extraction sections of the IA, 2D, and 3D Columns, and by the absorption of heat in the stripping columns IC, 2E, and 3E. Since uranyl nitrate is the Redox component transferred in largest amount in the process, its effect masks the heat effects resulting from the transfer of any other Redox process components. For the heats of extraction of Redox process components see Subsection B10,

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and for detailed data on the effect of temperature on mass transfer equilibria see Section C of this chapter.

1.26 Hydrogen ion concentration

If an aqueous solution of uranyl nitrate is in equilibrium with a hexone phase in a beaker, the addition of nitric acid to the system will alter the uranyl nitrate distribution. In general the presence of excess nitric acid in the aqueous phase has the effect of increasing the uranium distribution into the organic phase. This is due to the common ion salting effect of the nitrate ion formed by dissociation of the nitric acid.

A further consequence of the presence or absence of excess acid in the system is the effect on the pH. The hydrogen ion concentration in the aqueous phase may control the nature of the ionic or molecular species of a dissolved salt which in turn influences the distribution of the salt between the aqueous and hexone phases. Thus the transformation between uranyl ion and its dimer in aqueous solution is dependent upon the pH of the solution as indicated by the following equation: (6,47,52,72,126)

$$2UO_2^{++} + H_2O \rightleftharpoons U_2O_5^{++} + 2H^+.$$

The dimer ion is formed in aqueous solution above a pH of about 3, which is equivalent to about 0.025 M uranyl nitrate solution. The pH of the aqueous phase also influences the dissolved plutonium species (see Subsection B6), and therefore also the plutonium distribution in an aqueous-hexone system.

1.27 Oxidation state

The distribution of any metallic salt in an aqueous-hexone system varies with the state of oxidation of the cation. This may be illustrated by the following table for the distribution of plutonium into hexone from an aqueous phase 0.5 M in HNO_3 and saturated with amonium nitrate: (81)

Plutonium Distribution

Valence State	Distribution Ratio, E_a^o
III	0.14
IV	1.7
VI	9.8

The table illustrates the principle that generally the higher the oxidation state of a cation the greater is its organic solubility. Exceptions to the rule are Pu(V) and Np(V), which strongly favor the aqueous phase. Then if a reducing agent is added to a beaker containing an aqueous-hexone system at equilibrium with respect to Pu(VI), reduction of the plutonium causes a change in the Pu distribution ratio in favor of the aqueous phase. This is the basis for the separation of uranium and plutonium in the Redox IB Column where the plutonium oxidation state is lowered to the aqueous-favoring Pu(III) state while the uranium is unchanged. For detailed data on the

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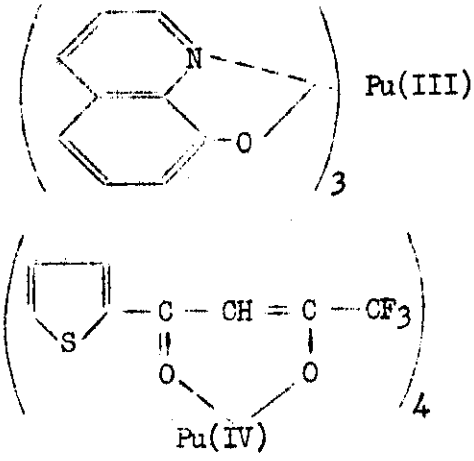
effect of the oxidation state on the distribution of the several Redox components, see Section C.

1.28 Complex formation

The addition of another substance to a liquid phase may increase, rather than decrease, the solubility of a solute in that phase. Thus it has been noted before that Pu(III) nitrate is relatively insoluble in hexone; however, the solubility may be greatly increased by the addition of 8-hydroxyquinoline which forms a hexone-soluble chelate complex with the Pu(III) ion. Then in a hexone-aqueous system, the organic-to-aqueous distribution ratio for Pu(III) may be increased by the addition of such a complexing agent to the system. During the early study of solvent-extraction processes for separating uranium and plutonium, considerable work was done on the addition of chelation compounds to organic solvents in order to increase the solvent solubility of plutonium.(100,103) Chelating or other special complexing agents were found to be unnecessary for operation of the Redox process with hexone as the solvent.

The structures of the organic soluble chelate complexes are indicated by the following formulas for the Pu(III) complex with 8-hydroxyquinoline and the Pu(IV) complex with thenoyl trifluoro acetone (TTA), which is used in plutonium analyses (see Chapter XX).



If uranyl nitrate is distributed at equilibrium between aqueous and hexone phases in a beaker, the addition of sulfate or phosphate ions to the aqueous phase shifts the uranium equilibrium in the direction of the aqueous phase.(18,45,58) This result may be interpreted as an increase in the relative solubility of the uranyl nitrate in the aqueous phase due to the formation of the sulfate or phosphate uranium complex. A similar effect is produced on plutonium distribution.(60) The presence of sulfate and phosphate ions is therefore generally undesirable during uranium and plutonium extraction. (However the high aluminum nitrate concentration (1.3M) in the IB

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Column is sufficient to overcome the effect of 0.05 M $SO_4^=$, which may be introduced as ferrous ammonium sulfate in conjunction with sulfamic acid, as reducing agent.)

1.3 Introduction to solvent-extraction

The recovery of uranium and plutonium from irradiated slugs by solvent-extraction involves (a) contacting the aqueous feed solution with hexone to permit the transfer of uranium and plutonium to the hexone phase, (b) separation of the phases after the desired mass transfer has taken place, and (c) separate recovery of the uranium, plutonium, and the hexone solvent. In the equilibration operation the hexone is referred to as the extractant and the hexone solution produced is the extract phase. The waste solution, from which the uranium and plutonium were extracted, is referred to as the raffinate phase.

As noted before, the extraction operation may be effected in the laboratory by mixing hexone with the aqueous feed solution in a beaker (or other convenient vessel such as a separatory funnel), then allowing the phases to settle or disengage. The mixing and settling operation represents an extraction "stage", and it is an ideal or theoretical stage if equilibrium between the phases ("phase equilibrium") is attained during the mixing and settling operation. The nearness of approach to phase equilibrium during a single mixing and settling operation is used as a measure of the efficiency of the stage. Multiple-stage countercurrent extraction may be effected by the use of an additional vessel for each additional extraction stage desired, by mixing and settling the two-phase system in each vessel, then transferring the phases in opposite directions through the series of vessels.

When the aqueous feed solution is extracted with hexone in the Redox process, the variables discussed under 1.2 (e.g., salting strength, pH, and cation oxidation state) are controlled to favor the extraction of uranium and plutonium while retaining the fission products in the aqueous phase. However, some fission-product transfer to the organic phase does occur. Such contamination of the hexone product stream is alleviated by contacting the organic extract with an aqueous salt solution under conditions which discourage the return transfer of the U and Pu to the aqueous phase while removing some of the fission products from the hexone solution. The operation is referred to as scrubbing, and the transfer contacts are referred to as scrub stages. Following the scrubbing of the extract phase, recovery of the hexone as well as the uranium and plutonium involves the transfer of the latter two components back to separate aqueous solutions. The plutonium is extracted by an aqueous reducing solution which removes the Pu as indicated in 1.27 but leaves the U to be stripped separately from the hexone solvent.

The mechanical methods of contacting and separating phases in solvent-extraction are described in detail in Chapter V. Since the rate of transfer of solute between phases is limited by the area of contact of the two phases, solvent-extraction equipment is designed to provide a large contact area. However, efficient operation requires rapid separation of phases as well as rapid transfer of solute, and is therefore dependent upon a compromise between fine dispersion to give maximum contact surface between

phases and coarse dispersion to give maximum rate of phase separation. For satisfactory operation the disengagement of a pair of contacted phases should normally be complete in less than a minute as indicated by batch contact results. Data on disengaging times may be found in Subsection B9 of this chapter, and the laboratory method of determining disengaging times is described in Chapter XX. The phase disengaging time is influenced by the pH of the aqueous phase; HNO_3 is sometimes added to Redox solutions to lower the pH and hence facilitate phase disengagement.

1.4 Determination of phase-equilibrium data

1.41 Methods

A number of methods are available for the laboratory determination of the mass transfer equilibrium data which are necessary for the evaluation of the performance of solvent-extraction equipment. The mass transfer occurring in continuous countercurrent extraction equipment may be simulated in the laboratory by the use of separatory funnels for perfect extraction stages. Thus twelve extraction stages may be simulated by twelve vessels in which the phases are contacted by shaking or by a mechanical agitator. When phase equilibrium has been reached within each stage, the phases are allowed to settle and then transferred countercurrently from one vessel to the next. By the addition of aqueous feed and removal of organic extract at one end of the series of stages, as well as the addition of hexone extractant and removal of aqueous waste at the other end of the battery, operation of the system may be continued until a steady state has been reached. At that point the composition of a given phase at a given stage does not vary appreciably with additional contacting and transfer of phases. When such a steady state has been realized, the solute distribution characteristics of the particular extraction system under study may be determined by analysis of all the phases throughout the series of vessels. The method is referred to in the Chemical Engineers' Handbook (8) and is described in detail in HW-14984.(173) Use of the method in shielded operations is described in KAPL-P-243. Uranium and nitric acid equilibrium data have been determined by this method and reported for the ANL June, 1948 Flowsheet(150), the ORNL June, 1949 Flowsheet(175), and the HW No. 4 Flowsheet.(173) The data are presented in Section C of this chapter.

Procurement of data by the above method is slow and requires a large amount of manual operation of the equipment. Much faster and simpler is the use of continuous mixer-settler contacting equipment such as that developed at the Knolls Atomic Power Laboratory(106,108,122) (see Chapter V). Such equipment is operated continuously by mechanical means until a steady state is reached. It is then possible to sample and analyze both phases in each stage. Such stagewise samples cannot be conveniently taken from a continuous column contactor.

1.42 Correlation of data

Correlation of the data obtained by phase analyses may be accomplished for a multiple-stage countercurrent system by plotting the solute concentration (uranium, plutonium, or nitric acid) in the hexone phase against the concentration in the aqueous phase for each stage, then joining the

points by a smooth curve. If the concentrations are expressed in terms of phase volumes (see Figure IV-48 for plutonium), then the slope of a straight line from the origin through any point on the curve represents the distribution ratio at that point. When the phase volumes do not remain constant during mass transfer (cf. uranium and nitric acid), equilibrium data are correlated by plotting concentrations in terms of the weight of the solute-free phase. This type of plot produces an equilibrium line such as that shown in Figure IV-36. For uranium the concentration is expressed in terms of the trihydrate (abbreviated UNT), because expressing the concentration in both phases in terms of the trihydrate results in a more nearly straight operating line than calculations in terms of the hexahydrate. For data on the state of hydration of uranyl nitrate in hexone see Subsection B3, and for detailed discussion of operating diagrams see Chapter V.

1.5 Solvent-extraction effectiveness

1.51 Physical factors

The physical factors influencing the effectiveness of a solvent extraction process are introduced only briefly here; they are discussed in greater detail in Chapter V in connection with Redox contactor operation. They are noted here to indicate their effect on the choice of chemical flowsheet conditions for the Redox process. The factors include temperature, interfacial tension, viscosity, density, and the ratio of the two phases contacted.

Raising the temperature at which phase equilibration is effected alters distribution ratios and increases the transfer rate by increasing the rate of thermal diffusion, decreasing interfacial tension, and decreasing viscosity. Lowered interfacial tension favors greater dispersion and therefore larger contact area, which results in undesirable emulsification in the extreme case. For data on the interfacial tension of Redox solutions see Subsection B9. It is to be noted that the concentration of a dissolved solute or the accumulation of insoluble foreign matter at an interface may reduce interfacial tension to the point of emulsification. Decreased viscosity of either phase of a two-phase system favors smaller droplet size of the dispersed phase. Diffusion rate and turbulence are also greater in a phase of lower viscosity. The greater the density difference between the phases, generally the less is the tendency for emulsification. Then for an aqueous-solvent system, the preference in the choice of a solvent will favor low interfacial tension, low viscosity, and low density. The use of contacting temperatures other than ambient has not shown sufficient advantage in the Redox process to be worth the added equipment complications.

Solvent-extraction efficiency is also influenced by the phase ratio, commonly referred to as the L/V ratio where L represents the weight or volume of aqueous phase per unit time and V represents the same for the organic phase. Weights of the solute - free phases are used when the mass transfer produces an appreciable change in phase volume (as in the case of uranium transfer); volume units are simpler to use when the phase volumes are largely unaffected by phase equilibration as is the case for

the plutonium-cycle columns. The L/V ratio expresses the slope of the operating line for a mass transfer process. For an extraction operation an increase in the operating line slope (raising the aqueous to organic phase ratio) increases the number of transfer stages required to effect a given separation as may be seen by reference to Figure IV-1. For a stripping operation the reverse is true. If it is assumed that, other factors being equal, the height of a perfect extraction stage remains constant, then increasing the number of stages necessitates increasing the height of the extraction section of a column contactor. Consequently, the choice of phase flow ratios for the Redox flowsheet depends partly, at least, upon a compromise between economical equipment requirements and economical solvent consumption. For a more detailed discussion of the derivation and use of operating diagrams, see Chapter V.

1.52 Measures of extraction performance

Several methods are available for calculating the effectiveness of a given separation process. The number of stages or transfer units required and the extraction factor are all measures of the difficulty of performing a given extraction. Calculation and use of these values are discussed in detail in Chapter V. The separation factor is a less commonly used quantity of value for comparing the effects of variables on the separation which can be achieved between two solutes in a particular mass transfer operation. It is expressed as the ratio of the distribution coefficients of two solutes being separated (see Figure IV-51 for the separation of uranium from fission products), and it is thus analogous to relative volatility as a measure of the ease of separation of components in distillation. The separation factor is also related to the decontamination factor (as shown in Figure IV-59) which is a measure of the effectiveness of the separation of a process component from fission-product contaminants and is calculated from laboratory data by dividing the measured counts per minute of a given weight of a component before and after processing. The decontamination factor is discussed in detail in Chapter I.

1.6 Chemical bases of the Redox process flowsheets

1.61 The Redox process system

The nitrate system was chosen because of the ease of dissolution of the slugs by nitric acid, the ready extractability of uranium and plutonium nitrates, and the less corrosive nature of the nitrate system as compared with a chloride system for example. Aluminum nitrate and ammonium nitrate both have advantages as Redox salting agents according to the requirements indicated under 1.24. The choice of aluminum nitrate over ammonium nitrate was largely based on the much greater stability of the former salt.

The selection of hexone as the solvent for the process was based largely on its availability, recoverability, and the fact that its selective solvent action met the decontamination requirements, as well as its general conformance with the other specifications indicated under 1.22. By way of example, the following table compares the density and viscosity of hexone with four other proposed solvents (see Sub-Subsection 1.51 and Chapter V

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for the effect of these properties on process operation)

	Specific Gravity, 20/20°C.	Viscosity, Cps. 20°C.
Ether	0.7146	0.25
Dibutyl carbitol	0.8853	2.39
Dibutyl cellosolve	0.8374	1.34
Triglycol dichloride	1.1974	4.93
Hexone	0.8042	0.59

Many other solvents have been tested experimentally, some of which show promise but are not readily available.

The steps in the Redox solvent-extraction system are described in detail in Chapter I including identification of each of the contactors and the entering and effluent streams of each. In simplified terms the process involves the following series of operations. In the 1A Column the aqueous feed solution is contacted with hexone to extract the uranium and plutonium from the bulk of the fission products; the hexone solution of U and Pu is then contacted with an aqueous aluminum nitrate solution to scrub out some of the fission-product contamination carried along with the uranium and plutonium. The hexone solution is next stripped of plutonium by contacting with a salted aqueous reducing solution in the 1B Column; the plutonium is thereby reduced to the hexone-insoluble Pu(III) state, while the uranium remains in the organic solution. The aqueous Pu solution is scrubbed with additional hexone to remove any uranium which may have been carried into the aqueous phase with the plutonium. Finally the uranium is stripped back into water solution in the 1C Column. The above outlined steps comprise the first Solvent-Extraction Cycle which accomplishes the separation of the uranium, plutonium, and fission products into three separate aqueous streams. Additional extraction, scrubbing, and stripping cycles are then carried out on the separate aqueous uranium and plutonium streams in order to effect further removal of contaminants from those streams. Subsections A2 through A12 discuss in detail the process chemistry of each column and related operations.

1.62 Acid and acid-deficient operation

It has been pointed out under 1.26, above, that free nitric acid has a salting action in the aqueous phase. The effect on the distribution of uranium into hexone is illustrated in Figure IV-31. However, raising the aqueous acid concentration increases the distribution of fission products into hexone at a greater rate than for uranium as is illustrated by the plot of the uranium-fission product separation factor illustrated in Figure IV-51. This relationship was the basis for the development of the acid-deficient Redox flowsheet to produce greater decontamination from fission products.

The Argonne National Laboratory (ANL) Redox flowsheets are acid flowsheets in which excess nitric acid is present in all streams (see Table IV-2 and Chapter I). The Oak Ridge National Laboratory (ORNL) Redox flowsheets are acid-deficient in the sense that neutral hexone is used for the organic extractant, and the aqueous streams in the uranium extraction

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cycles contain less than the stoichiometric amount of nitric ion required to balance the uranyl and aluminum ions after deducting sodium nitrate. Due to hydrolysis of the uranyl and aluminum nitrate salts, however, such a system still shows an acid pH. The Hanford Works (HW) Redox flowsheets are a hybrid combination of the ANL and ORNL flowsheets to utilize the advantages of both. In other words, the concentrated or product end of the uranium extractor is operated under acid-deficient conditions in order to achieve the highest possible decontamination of the product stream. On the other hand, the dilute or waste end is operated in the presence of excess nitric acid in order to utilize a higher distribution ratio for the attainment of lower waste losses (see Figure IV-33). This is achieved by addition of acid to the organic extractant stream, and is successful because it has been shown(31) that fission products transferred to the hexone under acid conditions are largely stripped back to the aqueous phase under acid-deficient scrub conditions, with the possible exception of ruthenium.(119)

1.63 Redox flowsheets

After establishment of the general Redox process pattern including the extractant and salting agent to be used, development of an optimum flowsheet requires correlation of the chemical variables discussed in Subsection 1.2 with the physical factors noted under 1.51. Of particular importance are the concentrations, acidities, phase flow ratios, and the oxidizing, reducing, and holding agents used. An optimum flowsheet should give the desired yield and purity of products with the minimum feasible volume of waste. The product specifications and the Redox process flowsheets designed to meet those specifications are discussed in Chapter I. For purposes of comparison, Table IV-2 summarizes the first-cycle chemical compositions for an acid, acid-deficient, and hybrid flowsheet. The chemical flowsheet variations are discussed in detail for each column in the following sections.

2. 1A Column

2.1 General principles

The primary function of the 1A Column is to separate uranium and plutonium from other transuranium elements and from fission products formed in the pile-irradiated metal. For transfer from the aqueous feed stream to the hexone extractant under acid-deficient conditions, the U and Pu must be in the (VI) valence state. In the operation of the Dissolver with excess uranium metal present at all times, the uranium is largely oxidized to the (VI) state by the nitric acid, while the Pu, being more difficultly oxidized, remains largely in the (IV) state. Therefore, feed preparation requires an oxidation step, as a result of which, excess oxidizing agent remains in the column feed. A small concentration is also added to the scrub solution to serve as a holding oxidant. Americium and curium cannot be oxidized above the (III) state in an aqueous acid medium,(11, 64) and therefore do not transfer appreciably to the organic phase, but instead are removed in the aqueous waste stream. Neptunium is fairly readily oxidized, and as a result, appears both in the product stream and in the waste stream, its distribution between these streams being dependent on the column operating conditions. The fission-product elements are more difficult to oxidize

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than U and Pu as a general rule, and consequently are more than 99 per cent removed in the IA Column raffinate.

The course of the IA Column streams is described in Chapter I. For flowsheet compositions of the entering and effluent streams see Table IV-2. The IAF:IAS:IAX flow ratio is 1:1:4, giving an aqueous-to-organic volume ratio of 1:2 in the extraction section and 1:4 in the scrub section.

2.2 Physical properties of the IA system

Since the transfer of uranium from the aqueous to the organic phase is exothermic, the temperature in the IA extraction system rises above room temperature. The highest temperature appears just below the feed point where the greatest mass transfer occurs, and there is a definite temperature gradient over the length of the column extraction section. Since there is little actual mass transfer in the scrub section, the only temperature effect in that section is the equilibration of the cool IAS stream with the warm hexone extract. For data on heats of extraction, see Subsection B10.

A large density gradient exists in both phases in the IA extraction section, whereas the scrub section shows little change. Table IV-25 shows the stagewise change in aqueous density as determined by laboratory countercurrent batch equilibrations for three typical flowsheets.

2.3 Chemical properties of the IA system

Higher valence states of the elements are generally more extractable by hexone than lower states (the V state being an exception). Uranium valence states below (VI) do not normally appear in the Redox system, and the plutonium (VI) state is at least as extractable as uranium (VI) under both acid and acid-deficient conditions.(20,123,198) Moreover, the interfacial transfer mechanism of uranyl and plutonyl nitrates is probably the same, and due to the similarity of the two compounds it is expected that such properties as the rate of diffusion are of the same order of magnitude although experimental verification has not yet been obtained. With these assumptions it is believed that the transfer-unit heights of the two components should be comparable, and the Pu losses should ordinarily be within specifications if the uranium losses are within the tolerance limits (provided the Pu is fully oxidized). Sodium dichromate is contained in both the feed and scrub streams in order to assure the retention of the Pu in the (VI) state. Actually Pu (IV) is also extractable but to a lesser degree than Pu (VI), and furthermore it tends to be unstable in an acid-deficient system with the formation of the Pu(IV) polymer (see Section B). Pu (V) is inextractable, but is readily oxidized to the (VI) state, indicating the need for a holding oxidant and for the absence of reducing impurities in the hexone extractant.

As indicated by the following table for batch extractions under both acid and acid-deficient conditions, americium is essentially inextractable in the Redox IA system:(116)

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Distribution of Americium

	Stream Compositions			Americium E_a^o
	IAF	IAS	IAX*	
(a)	2.0 M $UO_2(NO_3)_2$	1.3 M $Al(NO_3)_3$	0.5 M HNO_3	0.0018
	0.3 M HNO_3	0.004 M HNO_3		0.0017
(b)	2.0 M $UO_2(NO_3)_2$	1.95 M $Al(NO_3)_3$	Neutral	0.0029
	-0.2 M HNO_3	-0.13 M HNO_3		0.0030
	0.1 M $Cr_2O_7^=$	0.01 M $Cr_2O_7^=$		0.0032
				0.0024

*)The presence of 0.2 per cent methyl isobutyl carbinol in the hexone did not materially alter the distribution under acid-deficient conditions. While specific numbers are not available, curium is also believed to be as highly distributed into the aqueous phase in the IA system.

The oxidation-reduction potentials are such that the oxidation of plutonium to the (IV) state will also oxidize neptunium to the (VI) state in an acid medium.[70] However, the neptunium (VI) state is unstable under acid-deficient conditions (above pH 0.5) and is reduced to Np (V). Neptunium (VI) is slightly extractable[35,36] while in the (V) state neptunium is essentially inextractable.[39,132] Distribution ratios for oxidized neptunium have been reported as follows:[39]

Distribution of Neptunium

	Composition		Neptunium E_a^o
	Aqueous	Organic	
(a)	1.0 M $UO_2(NO_3)_2$	0.5 M HNO_3	1.4
	0.15 M HNO_3		
	0.7 M $Al(NO_3)_3$		
(b)	1.0 M $UO_2(NO_3)_2$	Neutral	0.02 to 0.03
	-0.2 M HNO_3		
	1.0 M $Al(NO_3)_3$		

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The smaller distribution ratio observed under the acid-deficient conditions is very likely due to partial reduction of the Np to the (V) state as well as to the effect of the acidity of the distribution of Np (VI). In the Redox IA system, neptunium will then follow both the IAP and IAW streams, and the portion following the product stream will be much smaller under acid-deficient than under acid conditions.

The use of a salting agent in the aqueous stream is necessary in order to obtain a satisfactory distribution of uranium and plutonium into the extractant. Of the many agents investigated(128), ammonium nitrate and aluminum nitrate have proved most satisfactory with hexone as the solvent.(91) Ammonium nitrate has yielded results indicating better decontamination, and because of its volatile cation it would probably be advantageous in disposing of the waste. However, aluminum nitrate has been found to be a satisfactory substitute which does not have the disadvantage of the instability of the ammonium salt.

The largest share of the decontamination in the Redox process is achieved in the IA Column, and is markedly influenced by the nitric acid concentration in the system. Acid-deficiency has the advantage of improved decontamination over a straight acid flowsheet for the IA Column. This applies to neptunium as well as fission products since in an acid-deficient system, the Np (VI) tends to be reduced to the aqueous-soluble (V) valence state. However, the reduced acidity also lowers the distribution of Pu and U into the organic phase. Compensation for this latter effect is achieved by increasing the salting strength, by operating the dilute end of the column under acid conditions in order to take advantage of higher distribution ratios (cf. the hybrid HW flowsheets), or by reducing the L/V ratio. As may be seen by reference to Table IV-2, the ORNL acid-deficient flowsheet and the HW hybrid flowsheet both show higher salting strength than the ANL acid flowsheet. The nitric acid relationships in the hybrid IA system are reviewed in HW-14984(173) and in KAPL-316.(119)

Sodium dichromate has been found to be the most satisfactory holding oxidant for use in the IA Column. However, the following table indicates that the plutonium entering the column at a valence state lower than (VI) will not be appreciably oxidized in the column:(118)

Rate of Oxidation of Pu (IV) to Pu (VI)

Temperature, °C.	Time Required to Oxidize Half of the Pu (IV)
25	No appreciable oxidation after 24 hours.
45	44 minutes
85	1 minute

Aqueous phase: 2.0 M $UO_2(NO_3)_2$, -0.25 M HNO_3, 0.1 M $Cr_2O_7^=$, 4.6×10^{-4} M Pu.

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For a detailed discussion of hexone impurities and their influence on the process, see Subsection B1. Deleterious impurities are largely removed from the organic streams by the hexone pretreatment operations. However, it may be noted here that impurities of a reducing nature, such as mesityl oxide(99), tend to convert plutonium to a less extractable lower valence state in the IA Column. Methyl isobutyl carbinol, present in raw hexone as an impurity of manufacture, complexes fission products into the hexone phase and therefore (particularly at acid flowsheet conditions) reduced decontamination if allowed to enter the IA system.

As may be seen by reference to Section C, an increase in the temperature of the two-phase system results in a lowering of the distribution of uranium and plutonium into hexone. The uranium transfer is exothermic and results in an appreciable temperature rise just below the feed point where the greatest transfer occurs. Under acid flowsheet conditions, however, no advantage is to be gained by lowering operating temperatures below normal room temperature in order to increase the uranium distribution into the organic phase, since the decontamination factor decreases by a factor of two when the temperature is lowered from 60° to 15°C. The principal effect of decreasing the temperature is to reduce slightly the number of stages required to attain a pre-determined waste loss limit.

Increasing the ratio of the aqueous phase to the hexone phase (L/V ratio, see Subsection 1.51 and Figure IV-1) produces several separate but related effects in the IA Column. If the L/V ratio is increased in the scrub section by raising the IAS flow rate, the reflux of all reversibly extractable components in the hexone stream is increased; the U and Pu concentrations in the IAP stream are thereby lowered. If the L/V ratio in the extraction section is raised by increasing the IAF flow rate or lowering the IAX flow rate, the product concentration in the IAP stream is raised. In addition, the higher ratio necessitates more stages in the extraction section in order to reduce the product concentration in the aqueous waste below the maximum permissible. On the other hand, decontamination is improved as may be seen by reference to curves D and E in Figure IV-59. The latter effect may be considered as due to the higher uranium concentration in the hexone phase back-salting fission products into the aqueous phase. Variation of the L/V ratio has an additional important effect on column operation when a hybrid flowsheet is being used. In this case the entering aqueous streams are acid deficient while the IAX hexone stream contains nitric acid. Then the balance between free acid and acid deficiency in the equilibrating system is just as dependent on the relative flow rates of the two phases as it is on the phase compositions. For example, either increasing the nitric acid concentration in the IAX, or reducing the L/V ratio by raising the IAX flow rate, will carry more nitric acid into the IA extraction section. Consequently the column would be operating with more acid extraction stages and fewer acid-deficient stages. The effect is to reduce both the waste losses sustained and the decontamination achieved. Hybrid flowsheet operation is thus sensitive to flow rate control.

2.4 Waste losses

The IA Column waste losses of uranium and plutonium are affected by the state of oxidation of each component, the acidity of the system, salting strength, and L/V ratio. In addition, the component concentration

in the feed stream may have an effect in unusual circumstances.

Uranium occurs in the Redox system only in the readily extractable (VI) valence state, and therefore presents no difficulty as far as oxidation state is concerned. However, plutonium can appear in lower oxidation states, and any appreciable proportion of Pu occurring below the (VI) valence state in the IA system is reflected in Pu losses in the IAW stream.

The acid balance in the column influences waste losses by the effect of excess nitric acid on U and Pu distribution ratios. Free nitric acid in the aqueous phase salts uranium and plutonium into hexone. In an acid-deficient flowsheet this factor shows little variability, while in an acid flowsheet the effect is largely dependent upon the acid concentrations of the feed streams. In a hybrid flowsheet on the other hand, the amount of free acid in the system is sensitive to relative flow rates as well as compositions (see the previous Subsection 2.3). If the L/V ratio is decreased by increasing the IAX flow rate with HW No. 4 Flowsheet compositions[193], the increased amount of nitric acid in the system increases the U and Pu distribution ratios (E_g); furthermore the slope of the operating line is reduced, thereby reducing the number of effective stages required to achieve a given recovery of uranium and plutonium.

Since the distribution of U and Pu into the organic phase increases with the salting agent concentration, any reduction in salting strength increases the number of extraction stages required to hold the waste losses below a specified maximum. This may be seen by reference to Figures IV-1 and IV-37, where it is apparent that lower salting strength gives a lower equilibrium line which in turn necessitates more stages to reach the given loss, X_w. Such a reduction in salting strength may occur not only by virtue of lowering aluminum nitrate concentration in the IAS stream, but also by decreasing the IAS flow rate relative to the IAF thereby producing greater dilution of the IAS salt stream by the unsalted IAF. Whether or not such a reduction in salting strength results in higher-than-flowsheet waste losses depends upon the spare extraction capacity built into the contactor. Thus if the stage height for a given system is 2 feet and the extraction section is 30 feet long, then increasing the number of stages required from 12 to 14 does not result in excessive losses since 15 stages are available.

Similarly, only if the extraction capacity of the system were being fully utilized would an increase in feed uranium concentration be reflected in increased U losses. It may be seen from Figure IV-1 that increasing the IAF uranium concentration places the starting point (X_f) of the extraction operation higher on the operating line, and more extraction stages are required to reach the waste loss goal. However, it is to be noted that fluctuations in the IAF uranium concentration are reduced in their effect on the point X_f by the dilution from the IAS stream. No serious effect, therefore, is generally produced on waste losses by small fluctuations of feed uranium concentration.

It should be noted that the determination of plutonium losses in the IAW stream by total alpha count requires a correction for americium and curium content. The latter elements are removed from the Redox system at this point. Their concentrations will vary with the pile power level and

exposure time, and must be accounted for by separate analysis.

2.5 Decontamination

The presence of excess nitric acid throughout the IA Column decreases the IA decontamination obtained and, conversely, the decontamination is improved by acid-deficient operation. In the case of hybrid flowsheet operation of the IA Column, acid extraction conditions at the bottom of the column cause distribution of some of the fission products into the hexone stream which is then partially decontaminated by the acid-deficient scrub section at the top. However, in this case, decontamination is somewhat less satisfactory than with totally acid-deficient operation since some fission products, particularly certain forms of ruthenium, are irreversibly extracted (see Subsection C4).

Methyl isobutyl carbinol, which is an impurity produced in the manufacture of hexone, tends to reduce decontamination by complexing cerium, niobium, and zirconium in the organic phase, under acid flowsheet conditions, though possibly not under acid-deficient conditions.(138) However, the MIBC is readily removed from the hexone by oxidation pretreatment (see Chapter IX).

Within the range of process concentrations (i.e., about 2 M aqueous aluminum nitrate or below), increasing aluminum nitrate concentration increases the separation factor slightly.(137) This may be seen by reference to Figure IV-51 which indicates that the uranium distribution ratio (E_D^o) increases with ANN concentration at a slightly greater rate than for fission products. This relationship holds for both acid and acid-deficient operation. The decontamination factor, however, under acid flowsheet conditions (0.2 M HNO_3 in IAFS), increases with an increase of $Al(NO_3)_3$ up to ca. 1 M in the aqueous phase and then decreases with additional $Al(NO_3)_3$. Under acid-deficient flowsheet conditions (~0.2 M HNO_3 in IAFS) the decontamination factor increases with an increase of $Al(NO_3)_3$ up to ca. 1.4 M in the aqueous phase before beginning to decline.

Uranium concentration has some influence on decontamination through the apparent effect of back-salting fission products from the hexone to the aqueous phase. This has been demonstrated particularly for cerium under acid extraction conditions.(111) A change in operation which increases the uranium concentration in the IAP stream (e.g., a decrease in the IAX relative flow rate) will then tend to improve the decontamination effected in the column scrub section.

For detailed data on fission-product distribution see Subsection C4. Decontamination results obtained in column operation are presented in Chapter V.

3. IB Column

3.1 General principles

The purpose of the IB Column is the separation of uranium from plutonium. This is accomplished by stripping the plutonium into an aqueous stream while retaining very nearly all the uranium in the organic stream received from the IA Column operation. The IB Column arrangement

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DECLASSIFIED

DECLASSIFIED

133

is similar to that of the IA in having an intermediate feed point, but is inverted in the sense that the extraction section (Pu stripping) is located in the upper portion of the column, while the aqueous plutonium stream is scrubbed in the lower portion of the column. The course of the IB Column streams is described in Chapter I. For the flowsheet compositions of the column streams see Table IV-2. With a IBF:IBS:IBX flow ratio of 420:200:40, a 10-fold concentration of the plutonium is effected in this column.

The plutonium is stripped from the organic phase, in spite of high aqueous salting strength, by reduction to the organic-insoluble Pu(III) valence state. The reducing agent is introduced in the IBX stream. At the same time the uranium is retained in the organic phase by virtue of the aluminum nitrate salting agent which is also present in the IBX stream. Neptunium is reduced to Np(IV) and is divided between the two effluent streams in a proportion which is very sensitive to the acidity in the column; high aqueous acidity favors distribution into the hexone. Fission products such as ruthenium are at least partly reduced to more aqueous-soluble forms, and are consequently divided between the uranium and plutonium streams.

3.2 Physical properties of the IB system

Since only a small amount of plutonium and uranium are transferred in the IB Column, there is little change in the density of the column streams as may be seen by reference to Table IV-2. However, a large loss of uranium in the IBP stream has the effect of slightly increasing the aqueous density. Flowsheet specifications permit a maximum concentration of 0.0006 grams of $UO_2(NO_3)_2 \cdot 6H_2O$ per liter in the IBP stream; this concentration would have to be increased 400-fold to produce an aqueous density increase of 0.0001 g./ml. Furthermore, the mass transfer is so small that no temperature gradient due to heat of extraction is observed in the column. Control of emulsification is effected by the slight excess of acid entering the top of the column in the IBX stream.

3.3 Chemical properties of the IB system

The four normal valence states of plutonium are represented by the ions Pu^{+3}, Pu^{+4}, PuO_2^{+}, and PuO_2^{+2}. The (III) and (IV) valence states, and the (V) and (VI) states, respectively represent reversible couples in which oxidation or reduction involves only the transfer of an electron. Transformation between one of the two higher and one of the two lower states involves the making or breaking of oxygen bonds and consequently tends to be a slower reaction. However, ferrous ion has been found to effect plutonium reduction sufficiently rapidly that the reaction may be completed during the normal residence time in the plutonium extraction section of the IB Column.(49,86)

The oxidation-reduction potentials of the principal heavy elements entering the IB Column are given in the following table:

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Element	Couple Potential, Volts (III)-(IV)	(IV)-(VI)
U	+0.63	-0.33
Np	-0.14	-0.94
Pu	-0.96	-1.0

According to the sign convention used in this table, higher algebraic value of a couple potential indicates stronger reducing power of the reduced form of the couple. Expressed in the form of an oxidation-reduction equation, such as:

$$U^{+3} = U^{+4} + e^- \quad (E_o = +0.63 \text{ volts}),$$

the higher algebraic potential of this couple indicates a greater tendency for U^{+3} to give up an electron and assume an algebraically higher ionic charge than the rest of the couples in the table. Then since the Fe(II)-Fe(III) couple has a potential of -0.77 volts, it may be seen that ferrous ion can reduce Np(VI) to Np(IV), that it can reduce both Pu(IV) and (VI) to Pu(III), and that it cannot affect uranium which will remain in the organic-soluble (VI) state. Since Pu(III) is not salted into the organic phase, essentially all the plutonium is then transferred to the aqueous phase. The yield of plutonium and the decontamination of uranium with respect to plutonium therefore depend on the completeness of the Pu reduction, and on the rate of the reduction. The time required for reduction under IB Column conditions has been found to be less than a minute.

It has been found that there is a tendency for the plutonium to be reduced in the hexone stream prior to contact with the IB Column reducing agent.(29,30) In the IA Column, reduction of Pu to the aqueous-soluble (V) state is prevented by the presence of dichromate, but partial reduction to the (IV) state may occur in the hexone after the IAP stream leaves the IA Column. However, this reduction does not take place in the absence of reducing impurities in the hexone.(86)

The ratio of hexone-insoluble Pu(III) to hexone-soluble Pu(IV) in the aqueous phase is dependent upon the ratio of ferrous to ferric ion, and may be expressed by the following equation:

$$\frac{Pu(III)}{Pu(IV)} = K \frac{Fe(II)}{Fe(III)},$$

where K is a proportionality constant.(86) Then in a hexone-aqueous system if it is assumed there is no Pu(III) in the organic phase, the plutonium distribution may be expressed by the following relationship:

$$E_a^o = \frac{Pu(IV)_{Org.}}{Pu(III)_{Aq.} + Pu(IV)_{Aq.}},$$

where the Pu symbols indicate the concentrations of the respective plutonium valence states in the organic and aqueous phases. Substituting for Pu(III) in the above equation we arrive at the relationship

DECLASSIFIED

DECLASSIFIED

135

$$E_a^o = \frac{E_a^o \text{ for Pu(IV)}}{1 + K\ Fe(II)/Fe(III)}$$

The constant, K, and the distribution ratio of Pu(IV) are fixed by the acidity and the salting strength of the system. Their values at various aluminum nitrate concentrations in 0.3 M HNO_3 in the aqueous phase are summarized in the following table:(118)

Aluminum Nitrate, M	Pu(IV) E_a^o	K
0.5	0.30	1800
0.9	1.0	500
1.3	8.4	360
1.5	50	320
2.0	--	250

Then for a given system the effect of the ferrous-ferric ion ratio on plutonium distribution may be calculated, and the results have been demonstrated experimentally.(88) Furthermore, if the Pu distribution ratio is calculated for a given ferrous-ferric ratio and it is assumed that the plutonium distribution remains constant at all process concentrations of Pu in the given system, then the plutonium equilibrium line for the system can be calculated from the distribution ratio and a given operating line (see Chapter V). It is also possible to calculate that a ferrous-ferric ratio of greater than one is required to reduce the plutonium losses in the IBU stream below 0.2 per cent for five extraction stages.

Ferrous iron is the most satisfactory IB system reducing agent which has been found. However, ferrous ion is thermodynamically unstable in the IB system and would normally be rapidly oxidized by atmospheric oxygen in contact with the IBX stream, or by nitric acid. Stabilization of the ferrous ion, however, is achieved by the addition of a holding reductant. Those reductants which are particularly effective in this role are capable of rapidly destroying any nitrous acid that may be present or which may be formed in the system. Many holding reductants have been tried with varying degrees of success. Among these are hydrazine, hydroxylamine, urea, and sulfamic acid, all of which contain an $-NH_2$ group capable of reacting with nitrous acid. Of these, hydroxylamine and urea do not react in the presence of hexone, hydrazine is toxic and tends to form a hexone-soluble ketazine complex with plutonium, while sulfamic acid is a readily obtained and easily handled solid which reacts satisfactorily. Pu(III), as well as Fe(II), is autocatalytically oxidized by nitrate ion.(1) The oxidation apparently involves nitrous acid, the destruction of which, prevents the autocatalytic reaction.(104) However, the nitrate oxidation of Pu(III) at room temperature is slow in the absence of a holding reductant.(76) The stabilizing sulfamate radical may be introduced into the system either as the ferrous sulfamate salt or as free sulfamic acid.

Sulfate ion may appear in the IB system either through the use of ferrous ammonium sulfate as the reducing agent, or as the result of hydrolysis of the sulfamate radical from ferrous sulfamate or sulfamic acid.

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However, the rate of sulfamate hydrolysis is slow at room temperature and at low free acid concentration.(104) The presence of sulfate in the system is a potential source of contamination of the IBP stream due to its formation of the aqueous-soluble uranium sulfate complex. However, it has been found that the effect is slight for sulfate concentrations below about 0.01 M, and that the effect is inhibited by excess acid, by aluminum nitrate, and by the presence if iron which appears to complex the sulfate preferentially.(57)

The acid content of the IB system is largely dependent on IA Column operation, since most of the nitric acid that enters the IB Column is contained in the IAP stream. However, a slight amount of nitric acid is added to the IBS hexone stream, and a slight excess of acid is generally used in preparing the ferrous reducing agent in order to prevent the precipitation of ferric hydroxide. This latter acid is consequently added to the IBX solution. Excess acid is desirable at the top of the column to accelerate phase disengagement. In addition, the IBP stream is potentially unstable under acid-deficient conditions because of the tendency for plutonium to precipitate as the oxalate in the presence of methyl isopropyl diketone impurity in the hexone. This is prevented by the addition of acid to the IBX stream.(31,67,79,80)

Raising the IBX flow rate to increase the L/V (aqueous-organic) ratio in the IB Column has the effect of reducing the concentration of the plutonium in the aqueous effluent, and of decreasing the decontamination of the Pu with respect to uranium. The relative flow rates must be a compromise between complete removal of the plutonium from the organic phase on the one hand, and concentration of the Pu without excessive carrying of uranium on the other. Decreasing the L/V ratio by increasing the feed rate increases the aqueous Pu concentration, but also increases the tendency for loss of Pu through incomplete reduction. Increasing the IBS rate only serves to lower the uranium concentration in the IBU, and since fission products are of secondary importance in this column, the scrub rate need only be sufficient to insure removal of U from the aqueous Pu stream.

Since uranium and plutonium distribution ratios vary with temperature at about the same rate, and since the rate of plutonium reduction is adequate at room temperature, there appears to be no advantage to be gained by operating the IB Column at other than room temperature.

The principal difficulty to be encountered from hexone impurities in the IB system is the adverse effect of oxidizing impurities. Mesityl oxide oxidizes ferrous ion, and if present in appreciable quantities it could thereby upset the plutonium distribution. It should be effectively removed by solvent treatment (see Chapter IX).

3.4 U and Pu recovery and decontamination

Uranium recovery is dependent upon sufficient salting strength in the aqueous phase, and on the number of scrub stages available. The number of scrub stages required is influenced by the L/V ratio. A large increase in the relative flow rate of the IBX stream with respect to the IBF stream increases the per cent of uranium in the IBP stream, and increases the number of stages required in the scrub section to effect 100

DECLASSIFIED

per cent reflux of the uranium back up the column. On the assumption that the distribution ratio is constant, with other factors equal, an increase in uranium concentration in the IBF stream increases the amount of uranium transferred to the aqueous phase. This potential loss is effectively offset by a slight increase in the IBS flow rate.

Plutonium losses in the IBU stream are not greatly affected by salting strength or acidity. The most important factor is efficient reduction through the maintenance of high ferrous to ferric ratio in the IBX stream and the presence of an adequate holding reductant to maintain this ratio during the column contact period. Decreasing the L/V ratio in the plutonium extraction (upper) portion of the IB Column has the effect of decreasing the opportunity for complete reduction of the Pu, as well as increasing the number of stages required for the transfer of the Pu to the aqueous phase.

Decontamination is of only secondary importance in the IB Column, and the fission products are about equally divided between the IBU and IBP streams. Neptunium largely follows the uranium under high acid conditions in the IB Column, but tends to be divided between the IBP and IBU streams as operating acidity is reduced.

4. IC Column

4.1 General principles

The purpose of the IC Column is to return the uranium to an aqueous solution largely free of plutonium and fission products. The stripping is accomplished by a simple extraction operation. For three typical flowsheet compositions of the IC Column streams see Table IV-2. With an aqueous-to-organic flow rate ratio of about 0.3, approximately a 3-fold concentration of the uranium is effected in the column. Further large reduction in the flow ratio is undesirable as too great a difference in flow rates produces a "pinch" between the equilibrium and operating lines at the concentrated end of the operating diagram; this causes excessive stripping stage requirements and high uranium losses.

Neptunium and plutonium are stripped into the aqueous phase along with the uranium. About a 10 per cent improvement in decontamination is effected in the column since irreversibly extractable fission-product elements leave the column with the ICW hexone waste stream. The majority of the fission products, however, follow the uranium. The ICW is directed to the IO Column and subsequent hexone recovery steps (see Chapter IX) before being recycled to the solvent-extraction battery.

4.2 Physical properties of the IC system

Flowsheet HW No. 4 stipulates a maximum uranium waste loss in the ICW stream of 0.05 per cent of the IA Column feed uranium, or about 0.07 grams of $UO_2(NO_3)_2$ per liter of ICW. Doubling this waste loss to 0.1 per cent of feed uranium increases the ICW density by about 0.0001 g./ml. Thus, while large uranium waste losses appreciably affect the ICW density, small deviations are not accurately determined by density measurements. The IC Column aqueous density profile has been calculated for the ANL and

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ORNL flowsheets[203], and stagewise densities determined by laboratory countercurrent batch equilibration are tabulated in Table IV-25.

The stripping of uranium from hexone to an aqueous phase involves the absorption of heat. Consequently there is a definite cooling of the IC Column streams with the lowest temperatures appearing at the point of greatest mass transfer in the column. For the heat of transfer of uranium in the IC stripping, see Subsection B10.

Under low acid conditions in the IC Column, emulsification of the phases tends to occur. This difficulty can generally be inhibited by the addition of 0.01 M HNO_3 to the ICX stream. For data on IC Column phase disengaging times, see Subsection B9.

4.3 Chemical properties of the IC system

The IC extractant is water to which a small amount (0.01 M) of nitric acid may be added if necessary to minimize emulsification. Since salting agent is absent, the uranium distribution highly favors the aqueous phase as is also the case with the neptunium and plutonium. This is true regardless of the state of oxidation of the Np and Pu when they reach the IC Column. The uranium remains in the (VI) valence state. The fission-product elements likewise largely follow the uranium in the absence of salting agent. For distribution data under IC Column conditions, see Section C.

As in the IB system the acidity of the IC Column is for the most part a function of the amount of acid carried over from the previous column operation. With acid-deficient or hybrid flowsheet operation of the IA Column, less than 0.04 M nitric acid is carried in the ICF stream. No acid is necessary in the ICX stream to strip the uranium completely, but, as has been noted, the addition of a small amount of nitric acid to that stream is desirable to minimize emulsification in such a low acid system. If the acidity of the system were to become extremely low at any point (pH above about 2.5), difficulty might be caused by the hydrolysis and dimerization of uranium according to the reaction:[47,124]

$$2UO_2^{+2} + H_2O \rightleftharpoons U_2O_5^{+2} + 2H^+ .$$

The possible stability and distribution of this dimer in the IC system are imperfectly understood. While the stream flow rates and uranium concentrations are essentially the same for acid, acid-deficient, and hybrid flowsheets, the nitric acid profile in the IC Column is decidedly different for the different flowsheets.

Since uranium distribution into the aqueous phase is favored by an increase in temperature, the lowering of the temperature of the system by mass transfer reduces the distribution into the aqueous phase in an adiabatic system, and necessitates additional stripping stages to achieve the desired extraction. In actual practice, heat transfer through the column walls may largely nullify the effect by raising the organic phase temperature to normal by the time it leaves the column at the top. Furthermore, the temperature effect may be readily counteracted by increasing the L/V

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ratio (increasing the slope of the strip operating line) which decreases the number of stages required to achieve a given waste loss limit. For the effect of temperature on uranium equilibrium in the IC system see Figure IV-34.

Decreasing the aqueous/organic flow ratio, by increasing the organic or decreasing the aqueous flow rates, results in increased concentration of the uranium in the aqueous phase. Additional stripping stages or transfer units will then be required to reduce the uranium waste loss in the ICW stream. Concentration of the uranium in the IC Column is desired because 2 M uranium solution is required for feed to an additional uranium extraction and stripping decontamination cycle. At high aqueous concentrations, however, the distribution ratio (E_a^o) of uranium becomes unfavorable. The IC Column flowsheet then represents a compromise between minimum stripping transfer units (high aqueous flow rate and short column), low uranium waste losses (low aqueous uranium concentration), and stream stability (aqueous and organic flow rates of the same order of magnitude) on the one hand, and high aqueous uranium concentration for second cycle feed on the other.

4.4 Losses and decontamination

Decontamination in the IC Column is of secondary importance, and is largely a function of which fission products follow the uranium from the IB Column. The Pu(IV) polymer is only slightly extractable by hexone; however, if any polymer has been formed earlier in the system and transferred to the organic phase, it is stable in the organic solution and is removed with the ICW stream. It therefore constitutes a Pu loss, but does not contaminate the uranium. However, normal plutonium (uncomplexed) and neptunium follow the uranium in the IC system. Some fission-product elements are also stable in the organic phase, particularly certain forms of ruthenium, and are therefore eliminated in the ICW. Most of the fission products follow uranium (cf. HW-14261(169)).

High aqueous acidity causes poor stripping by salting uranium into the organic phase. However, fluctuations in aqueous acid concentration in the flowsheet range of 0 to 0.1 M has little effect on uranium waste losses in the IC Column except for its influence on possible entrainment of aqueous solution with the ICW. An increase in the concentration of uranium in either the ICF or ICU requires additional transfer units to achieve a given waste loss, as does a decrease in the aqueous-to-organic ratio, L/V. Temperature fluctuations over a range of 15°C. in the IC stripping operation do not produce an appreciable effect on waste losses.

5. ICU Concentration

5.1 Relation to the process

As the ICU stream comes from the IC Column, it contains U(VI), Pu(VI), Np(IV), and the fission-product elements Ru, Nb, Zr, and Ce in that general order of abundance.(169) Additional decontamination of the uranium may or may not be required at this point, depending upon the ultimate use and method of handling the recovered uranium, and on the

decontamination achieved in the feed preparation and the first solvent-extraction cycle. Such additional decontamination is effected by the second (and third, if necessary) extraction and stripping cycles. The maximum feasible concentration of uranium in the ICU stream is about 0.8 M, while high aqueous uranium concentration (2 M) is prescribed by the flowsheet for 2DF feed to the second uranium cycle. Therefore, concentration of the ICU is necessary if further decontamination is required. Concentration of the feed stream, rather than the aqueous waste stream from a new extraction cycle, reduces the salting agent requirements and consequently reduces the final aqueous waste volume attainable.

The aqueous ICU stream is saturated with hexone as it comes from the IC Column. In addition, it may contain up to 0.1 or 0.2 M HNO_3 under hybrid or acid-deficient flowsheet operation. Elevated temperature evaporation of water from the ICU stream as it comes from the column would then introduce the possibility of nitrate or nitric acid oxidation of the dissolved hexone. Such oxidation yields degradation products, e.g., methyl isopropyl diketone and oxalic acid, which have an adverse effect on subsequent solvent-extraction operations (see Subsection B1). To obviate this eventuality the hexone must be largely stripped (ca. 95 per cent) from the aqueous solution prior to uranium concentration. Furthermore, the solution must be neutralized with caustic to provide an acid-deficient feed for a subsequent uranium decontamination cycle.

5.2 Method of continuous concentration

In order to effect hexone removal prior to aqueous concentration, the ICU stream is continuously introduced at an intermediate point in the concentrator column, and the hexone is then steam stripped from the aqueous stream as the latter flows down the column to the distillation pot.

Neutralization of the aqueous uranium stream is accomplished on a continuous basis by the addition of liquid caustic to the ICU Concentrator pot. The concentrate is continuously removed from the concentrator, cooled, and fed to the 2D Column. The uranium flow is therefore continuous from the initial extraction to the final decontaminated stream.

See Section B of this chapter for specific properties of the concentrator system: vapor-liquid equilibrium, density, boiling point, specific heat, and viscosity.

6. 2D Column

6.1 General principles

After the preparation of acid-deficient 2 M uranyl nitrate solution in the ICU Concentrator, the concentrate is fed as the 2DF stream to an intermediate point in the 2D Column. This column is a compound contactor similar to the IA Column, and its purpose is to separate uranium from plutonium as well as from neptunium and fission products.

Operation of the column is analogous to the IA in that the continuous phase is aqueous while the hexone extractant is dispersed. The 2DX hexone stream enters the bottom of the column, rises through the extraction section,

DECLASSIFIED 141

and is finally contacted above the feed point by the aqueous scrub solution (2DS) which enters the top of the column. The uranium-bearing hexone leaves the top of the column as the 2DU stream, and the aqueous raffinate leaves the bottom as the 2DW stream.

The principal difference between the IA and 2D Columns is that the latter is required to separate plutonium as well as other impurities from the uranium. Consequently, the 2DS stream contains both ferrous ion, to reduce the plutonium to the organic-insoluble (III) state, and aluminum nitrate, to salt the uranium into the hexone. A holding reductant is also required.

6.2 Physical properties of the 2D system

The production of a temperature gradient in the 2D Column, as a result of the evolution of the heat of extraction of uranium, is the same as noted for the IA Column. Since the flow rates and concentrations are the same as in the former case, the effect is quantitatively the same.

The variation of aqueous density through the column is likewise the same as for the IA system. Similarly, variation of the 2DW density with waste losses will amount to about 0.0006 g./ml. for a change of 0.78 g./l. in the $UO_2(NO_3)_2$ waste concentration.

6.3 Chemical properties of the 2D system

Plutonium enters the 2D Column in the (IV) and (VI) valence states, but is held in the aqueous phase by reduction to the (III) state by Fe^{+2}. Any neptunium present in higher valence states is converted to aqueous-favoring Np(IV) by the ferrous ion. The transuranium impurities are thus removed via the 2DW stream, while the uranium is transferred to the hexone phase.

The most effective reducing agent and holding reductant are those used in the IB Column, Fe^{+2} and sulfamate ion. The sulfamate serves another purpose in addition to stabilizing the ferrous ion in the system. It has been reported that nitrous acid increases the distribution of ruthenium into the organic phase.(130) Therefore the presence of sulfamate in the 2D Column should improve ruthenium decontamination if any nitrite is produced in the ICU concentration step (see GE-H-13120(95) and Subsection C4).

The aluminum nitrate salting strength is the same as in the IA system. The optimum fission-product decontamination is achieved by acid-deficient operation in the upper portion of the column, whereas uranium waste losses are minimized under HW No.4 Flowsheet operation by the introduction of acid in the 2DX stream at the dilute end of the column.

Flow ratio variations will produce the same effect as already described for the IA Column; i.e., a lower L/V ratio means a lower operating line slope and a smaller extraction factor. Consequently, fewer stages are required to attain specified waste losses when the L/V ratio is reduced in the extraction section. On the other hand, increasing the ratio tends to improve decontamination. Typical flowsheet flow rates and com-

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positions for the 2D Column are summarized in Table IV-2.

6.4 Waste losses

Uranium waste losses in the 2D Column are dependent entirely on the operational variables. The uranium is in the organic-soluble (VI) valence state, and is satisfactorily extracted provided sufficient extraction stages are available by: sufficient salting strength which means maintenance of the 2DS flow rate relative to the 2DF stream, excess nitric acid at the dilute end of the column, and the minimum operating line slope consistent with the requirements of the system.

6.5 Decontamination

Practically 99 per cent of the plutonium which enters the 2D Column leaves with the 2DW stream. The neptunium concentration is reduced by a factor of approximately 20, which is adequate neptunium separation even if all the neptunium in the Redox feed solution followed the uranium in the IB Column. Fission-product decontamination is dependent upon the same variables as discussed for the IA system. However, the actual decontamination achieved in this column is much less than in the IA Column due to the fact that the more easily separable fission products have already been removed as well as the fact that the initial concentration here is much lower.

7. 2E Column

7.1 General principles

The 2E Column is a simple column similar to the IC. The organic feed, 2EF (the 2DU stream from the 2D Column), enters the bottom of the column and rises as the dispersed phase. The uranium is stripped into the aqueous phase by the extractant, 2EX, which enters at the top of the column. The effluent uranium is thus in the form of an aqueous solution suitable for metal recovery or an additional decontamination cycle if necessary. The plutonium content is negligible at this point, the neptunium has been more than 50 per cent removed, and fission-product radioactivity has been reduced to about 5.6×10^{-5} countable curies of gross beta radioactivity/gal. and 5.1×10^{-6} countable curies of gross gamma radioactivity/gal.

7.2 Physical and chemical properties of the 2E system

In operation and function this column is similar to the IC Column, the chief difference between the two being the greater L/V ratio in the 2E Column. This is both necessary and desirable because of the fact that the organic feed solution to the 2E Column (the 2DU stream) has a higher uranium concentration than that of the ICF stream. This difference arises from the addition of the IBS scrub stream to the organic phase from the IA Column, while no such operation is necessary in the case of the second uranium decontamination cycle. The higher relative aqueous flow rate in the 2E Column produces essentially the same aqueous uranium concentration as the IC Column due to the higher feed concentration in the former case.

DECLASSIFIED

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As in the case of the IC Column, the addition of a small amount of acid to the aqueous extractant may be desirable for its effect on decreasing the disengaging time at the top of the 2E Column. Otherwise, the 2E acidity is dependent upon the acid carry-over from the 2D Column. Due to the difference in flow rates and feed concentration, the density profile of the 2E Column is different from the IC Column, but the variation of the organic effluent density with uranium waste losses will be the same as for the IC system. Since the amount of uranium being transferred per unit time in the 2E operation is the same as in the IC, the heat absorption effect is the same in the two systems. The effects of variations in the L/V ratio are essentially the same as those for the IC operation.

7.3 Losses and decontamination

Decontamination is of secondary importance in this column and amounts to a factor of about 2. Residual radioactivity is so low at this point that proper determination of the decontamination achieved involves a necessary correction for the presence of U^{237} beta and gamma radioactivity.(138) Otherwise losses and decontamination are dependent upon the same factors as for the IC Column.

8. Third Uranium Decontamination Cycle

8.1 General principles

A third decontamination cycle may be necessary, depending upon the results achieved in the previous operations as well as the ultimate consignment of the uranium. This third cycle is available in the Redox plant but will not be used unless necessary.

8.2 Physical and chemical properties of the system

As may be seen by reference to Chapter I, the third-cycle flow rates, compositions, and operations, are essentially the same as the second. The operations involve the concentration of the 2EU stream in the same manner as the ICU, the transfer of the uranium to hexone, and scrubbing with aluminum nitrate solution in the 3D Column, followed by the return of the uranium to an aqueous solution in the 3E Column. The nitric acid concentration is lower in the 2EU stream than in the ICU stream, and consequently less caustic is consumed in the 2EU concentration. The overall decontamination achieved must again be corrected for U^{237} radioactivity in the 3EU stream.

8.3 3EU concentration

Concentration of the final aqueous uranium solution is necessary whether one, two, or three decontamination cycles are required. The function of the final concentration is to strip out the dissolved hexone as well as to remove part of the water in preparation for conversion of the uranyl nitrate to uranium trioxide. Just as in the ICU concentration, hexone removal is necessary to prevent the formation of hexone degradation products. The operation is completely comparable to the ICU and 2EU concentration steps.

DECLASSIFIED

9. Cross-Over Oxidation

9.1 General principles

The cross-over oxidation is the operation which couples the first-cycle plutonium decontamination with subsequent plutonium decontamination cycles. The separation of plutonium from uranium in the IB Column yields an aqueous solution of Pu(III), the IBP stream. Additional Pu decontamination requires oxidation of the plutonium to a hexone-soluble valence state. This conversion of Pu(III) to Pu(IV) and/or Pu(VI) is accomplished in the cross-over oxidation step.

Pu(III) is more readily and rapidly oxidized to Pu(IV) than to Pu(VI) since the former transformation requires only an electron transfer, while the latter involves the formation of oxygen linkages to yield the plutonyl ion. Pu(IV) is less soluble in hexone than is Pu(VI), but in the presence of excess acid Pu(IV) has a satisfactory distribution ratio for hexone extraction. It is doubtful whether very much greater decontamination can be attained by acid-deficient extraction of Pu(VI) than by acid extraction of Pu(IV). Therefore, it is more advantageous to use the rapid oxidation of plutonium to the (IV) valence state followed by acid extraction, rather than the slower oxidation to the (VI) state and acid-deficient extraction. Potential plant capacity is greater with the faster oxidation system.

The cross-over oxidation may be effected either in a batch process or by continuous operation.(180) Since Pu(III) is much more rapidly oxidized to the (IV) state than to Pu(VI), the use of Pu(IV) in subsequent extraction is particularly desirable for continuous operation. Such a continuous process is more desirable from the standpoint of both operational and critical mass control. The continuous oxidation may be carried out as a separate operation between the IB and 2A Columns, or it may prove feasible merely to add the oxidizing agent to the 2A Column scrub stream and rely on oxidation of the Pu(III) to Pu(IV) within the 2A Column.

The batch reaction may be carried out hot or cold. Hot oxidation necessitates the prior removal of dissolved hexone from the aqueous Pu solution in order to prevent the formation of hexone decomposition products which are detrimental to subsequent Pu extraction and stripping operations.(39) Particularly undesirable is the oxidation of hexone to methyl isopropyl diketone, since the diketone in the presence of Pu(IV) can be converted to oxalate which precipitates Pu(IV).(39) The Pu(V) state has not been observed in the cross-over oxidation system.

The cross-over oxidation step must also oxidize the ferrous ion reducing agent which accompanies the plutonium from the IB Column. Sulfamate ion, from either sulfamic acid or ferrous sulfamate IB holding reductant, is unaffected by oxidizing agents.(177) However, excess acid and elevated temperatures accelerate the hydrolysis of the sulfamate ion to ammonium and sulfate ions (cf. Subsections B7 and B8).

Oxidation under acid conditions will convert neptunium to the organic-soluble (VI) valence state(70), but under acid-deficient conditions, above a pH of about 0.5, the (VI) valence state is unstable and is reduced to Np(V) which is inextractable.(39,41,132)

DECLASSIFIED

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The choice of an oxidizing agent is at least partly based on its oxidizing potential which should be sufficient to produce the desired plutonium valence state. Since a clarification step is extremely undesirable, solids formation cannot be tolerated in the oxidation step. Possible oxidizing agents[26] include dichromate ion[185], ozone[177], permanganate ion[22], ceric ion[151,152], and hydrogen peroxide[22,76]. For the stability of the Pu valence states, see Subsection B6.

9.2 Dichromate oxidation

9.21 Rate

The oxidation of Pu(III) to Pu(IV) and of Fe(II) to Fe(III) by dichromate is very rapid, the reaction being complete in less than 20 seconds at 25°C. The oxidation of plutonium to Pu(VI) is much slower, a half-time of 20 hours having been observed for the oxidation of the plutonium in an ANL Flowsheet IBP stream in the presence of hexone.[185] The latter reaction, however, may be accelerated by the influence of other variables.

9.22 Concentration of Dichromate

The oxidation of Pu(III) is sufficiently rapid with the use of the approximate stoichiometric amount of dichromate required to complete the oxidation of the Fe(II) and Pu(III) in the IBP stream. Since the presence of an appreciable excess of dichromate adversely affects decontamination in the 2A Column, no advantage is to be gained by the use of greater than flowsheet concentrations (0.01 M) of dichromate.

9.23 Nitrate ion concentration

The oxidation rate of plutonium decreases with an increase in nitrate ion concentration when the acidity, ionic strength of the solution, and dichromate concentration, remain constant. This effect is probably due to the formation of Pu(IV) complexes such as $Pu(NO_3)_3^+$ or $Pu(NO_3)_6^=$, which are oxidized more slowly than hydrated Pu(IV) ion itself.

9.24 Hydrogen ion concentration

Acid is consumed in the oxidation as indicated by the following equation:

$$6\ Fe^{+2} + Cr_2O_7^= + 14H^+ \rightarrow 6Fe^{+3} + 2Cr^{+3} + 7H_2O.$$

The oxidation of 0.05 mole of Fe^{+2} will consume 0.117 mole of acid and about 0.008 mole of dichromate. An increase in the acidity of the solution will then accelerate the rate of the reaction.

The oxidation of Pu(III) to the (IV) and (VI) states also consumes acid, as shown by the following over-all reactions:

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$$6Pu^{+3} + Cr_2O_7^{=} + 14H^{+} \longrightarrow 6Pu^{+4} + 2Cr^{+3} + 7H_2O;$$

$$2Pu^{+3} + Cr_2O_7^{=} + 6H^{+} \longrightarrow 2PuO_2^{+2} + 2Cr^{+3} + 3H_2O.$$

Due to the small concentration of plutonium in the solution, the amount of acid required in comparison with ferrous iron is negligible. At low hydrogen ion concentrations, however, the oxidation of Pu(IV) to the (VI) valence state is also hindered by hydrolysis of the Pu(IV). It is to be noted that the rate of oxidation of Pu(IV) to Pu(VI) is decreased by increasing nitric acid concentration. This effect is probably produced by the complexing action of the nitrate ion.

9.25 Catalysis

A variety of dichromate oxidizable substances are catalysts for the oxidation of Pu(IV) by dichromate. The accelerating agents may either act as true catalysts, or as inducing agents which produce intermediate chromium states that are more rapid oxidants than the dichromate itself. Tested catalysts in order of decreasing effectiveness are ethanol, hydrazine, Mn(II), hexone with sulfamic acid, Co(II), Fe(III), and Ce(III). However, the Redox flowsheet does not specify the use of a catalyst since oxidation beyond Pu(IV) is not required. The 2A Column is designed to extract all the Pu(IV) that might be present.

9.26 Effect on decontamination

The presence of excess dichromate in an acid 2A Column adversely affects cerium decontamination, and also that of zirconium in the presence of methyl isobutyl carbinol.(105,118) Improvement in 2A Column decontamination may then be effected by the addition of just sufficient dichromate to oxidize Pu(III) to a mixture of Pu(IV) and (VI). The gross beta-gamma distribution ratio is doubled by doubling the amount of dichromate used to accomplish the oxidation to the higher mixed valence states, and thus adequate control is required to reach the proper equivalence point.(107)

9.27 Effect of Hexone

Hexone decomposition products accelerate the rate of Pu oxidation more than hexone itself, and the rate of oxidation of new solutions containing hexone increases as hexone decomposition products are formed. The formation of hexone decomposition products can have a deleterious effect on the subsequent plutonium decontamination cycles, both by increasing fission-product distribution into the organic phase, and by the precipitation of plutonium (IV) oxalate. The danger, of course, is exaggerated if hexone is present as a second phase due to entrainment or flooding in the lower portion of the 1B Column. When elevated temperature is utilized in the cross-over oxidation, prior stripping of the hexone is required.

DECLASSIFIED

9.3 Other oxidants

9.31 Ozone

Ozone oxidation(177) has the advantage of improved decontamination, as well as the elimination of the introduction of additional interfering ions in the 2A Column, which simplifies re-processing off-standard streams. The cerium distribution from an ozonized solution is reported as 0.0002 (E_a^o); from the same solution oxidized with 0.02 M dichromate the distribution ratio is reported as 0.87.(177)

Laboratory ozonolyses have been performed without removing the hexone, but this practice introduces a potentially hazardous reaction between the hexone and ozone. Also, the presence of hexone inhibits the plutonium oxidation, and its presence results in the formation of methyl isopropyl diketone. In ozonolyses performed by an oxygen stream containing 2.5 volume per cent ozone, the flow ratio of 200 volumes of gas to 1 volume of solution per hour oxidizes plutonium completely to the (VI) state in less than one hour at 75°C., and in less than six hours at 25°C. A 0.01 M solution of silver nitrate is used as a catalyst. Higher temperatures or longer reaction times are necessary in the absence of the catalyst. The Pu(VI) obtained by ozonolysis is reduced at a rate of 0.33 per cent per day when neither hexone nor holding oxidant is present, but the rate is increased to 2 per cent per day in the presence of hexone. Ozone is therefore not a desirable oxidant since the oxidation rate is slow and the higher valence state is not stabilized.

9.32 Hydrogen peroxide

The use of hydrogen peroxide(151,152) for the cross-over oxidation has advantages similar to ozone. Oxidation with twice the concentration of peroxide necessary to destroy the ferrous ion gives about equal amounts of Pu(IV) and Pu(VI); four times the amount required to destroy Fe^{++} gives mostly Pu(VI). The reaction is accompanied by effervescence from peroxide decomposition. The disadvantages of hydrogen peroxide are its slow reaction rate and its tendency to precipitate plutonium peroxide. At low acidities a portion of the plutonium forms a peroxide colloid. Peroxide oxidation in the presence of hexone results in the formation of colored organic materials.

The distribution of cerium from peroxide-oxidized solutions is 0.0014 (E_a^o), which is less than that for 0.02 M dichromate-oxidized solutions.(154) Ruthenium distribution is of the same order of magnitude by either means of oxidation.(152) Sodium peroxide gives similar results but is difficult to handle.

9.33 Permanganate-peroxide

The use of a combination of permanganate and peroxide is lengthy and complex, and there is also the potential difficulty of manganese dioxide precipitation. The procedure involves the addition of permanganate and air sparging, followed by the addition of hydrogen peroxide. The use of sodium permanganate results in formation of an unidentified precipitate

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which is not obtained with the potassium salt. Beta decontamination obtained in column runs following this method of oxidation were lower than those using ozone or dichromate.

9.34 Ceric ion

Ceric ion may be used as a catalyst for ozone or dichromate oxidation of plutonium, but being a strong oxidant it also oxidizes the fission-product elements thus resulting in poor decontamination in the subsequent extraction cycle. In a solution 0.5 M HNO_3, oxidation to Pu(VI) is complete in less than 10 minutes. Hexone, if present, is also oxidized, but at a slower rate. Solutions oxidized by ceric ion showed a distribution coefficient (E_a^o) of 0.44 for ruthenium tracer, as compared with 0.064 for comparable solutions oxidized with dichromate.

10. 2A Column

10.1 General principles

The second and third plutonium decontamination cycles are carried out in the 2A-2B and 3A-3B Column systems respectively. The 2A Column in the second plutonium cycle is analagous to the IA Column in the first-cycle operation; its purpose is to decontaminate the plutonium further by extraction into hexone, leaving the fission products in the aqueous waste stream. The 2AF stream is fed to the column at an intermediate point and flows to the bottom as the continuous phase. The extractant stream (2AX) is introduced at the bottom, and ascends as the dispersed phase to the upper portion of the column where it is scrubbed by the 2AS stream entering at the top. Typical flowsheet stream compositions and flow rates are summarized in Table IV-2.

As in the case of the IA Column, the 2A Column may be operated under acid, acid-deficient, or hybrid flowsheet conditions. Acid-deficient or hybrid operation necessitates oxidation of the plutonium to Pu(VI) in the cross-over oxidation in order to get satisfactory extraction in the 2A Column. Since, as noted in Subsection 9 , above, it is more desirable not to carry the plutonium oxidation completely to Pu(VI), it is then necessary to utilize acid extraction in the 2A Column. Furthermore, it is doubtful whether acid-deficient operation would produce an appreciable improvement in 2A Column decontamination.

10.2 Chemical properties of the 2A system

The extraction of Pu(IV) and of Pu(VI) have both been suggested as bases for the operation of the 2A Column. Operation with Pu(IV) has the advantage of simplifying the plutonium cross-over oxidation and of retaining the fission-product elements in the less extractable lower valence states. The advantage tends to be counterbalanced by the fact that the Pu(IV) is less extractable than Pu(VI), which thereby requires higher salting strength, lower L/V ratio, or greater column length in order to reduce Pu waste losses to an acceptable level. Actually the 2A Column is designed to extract Pu(IV) adequately. A slight excess of dichromate is present in the 2AF stream and in the 2AS stream to serve

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as a holding oxidant for the plutonium in the column. For plutonium distribution data, see Section C.

The principal fission products which reach the 2A Column with the plutonium stream are cerium, ruthenium, and zirconium. The first two are sensitive to the oxidizing conditions in the cross-over oxidation and have a tendency to be transferred into the extract stream. The zirconium is ordinarily adequately removed, but, as noted before, appears to be particularly susceptible to the effect of solvent impurities (e.g.,MIBC).

The aluminum nitrate salting strength in the extraction section is considerably higher than that used in the IA Column because of the absence of the salting effect of the uranium present in the IA system. Approximately half of the aluminum nitrate employed reaches the 2A Column by way of the aqueous plutonium extractant stream from the IB Column, as a consequence of which the salting concentration requirement in the scrub section is markedly lower than in the IA Column. The lowered scrub salting strength has the effect of increasing the plutonium reflux in the column, but also tends to improve removal of fission products from the organic stream.

The 2A-2B system is sensitive to nitric acid concentration throughout the cycle. Raising the acidity in the 2A Column improves the plutonium extraction, but it results in a higher acid concentration in the 2AP stream which increases the difficulty of stripping the plutonium to the aqueous phase in the 2B Column. The amount of acid introduced into the 2A system is therefore a compromise between the two opposing factors resulting in a comparable number of transfer stages (comparable heights) for the two columns.

Variations in the L/V ratio have the same general effects as in the IA Column. Since the actual mass transfer taking place in the system is slight, extraction produces no appreciable effect on stream densities, and no appreciable heat of extraction is observed. Small variations in operating temperature are not likely to alter the decontamination achieved, since the distribution ratios of all of the components of the system vary with temperature in about the same fashion, and changes in stage heights with temperature should be about the same for all components.

10.3 Waste losses

Any variation in the ratio of the 2AS and 2AF stream flow rates does not greatly alter the salting strength of the aqueous phase in the extraction section, since both streams carry about the same concentration of aluminum nitrate. A reduction in salting strength or excess acid in the extraction section, however, must be counteracted by a decreased L/V ratio, if the plutonium waste loss is to be maintained below the allowable maximum.

Any americium carried over from the first-cycle operation is eliminated in the 2AW stream, and a correction for its presence must be made in the determination of Pu waste losses by total alpha count. For the plutonium extraction stage and transfer-unit requirements in the second and third plutonium cycles, see Chapter V and HW-19047.(190)

DECLASSIFIED

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10.4 Decontamination

The operational variables affecting decontamination in the 2A Column are the same as those for the IA Column. The actual decontamination accomplished in the 2A Column, however, is much less than for the IA system because the easily separable fission products have already been removed.

11. 2B Column

11.1 General principles

In the 2B Column the plutonium is transferred to the aqueous phase, and is then available for further decontamination or for processing to metal. Decontamination in the column is of secondary importance, and most of the radioactivity present in the system follows the plutonium. This is a simple column and uses the 2AP stream as feed (2BF), entering at the bottom. The aqueous extractant (2BX) enters the column at the top and flows to the bottom as the continuous phase. The stripping of the plutonium into the aqueous phase is analagous to the uranium stripping in the IC, 2E, and 3E Columns. No change in the plutonium valence state is required, which differentiates the operation from the IB Column plutonium extraction.

11.2 Column chemistry and operational variables

The only chemical changes occurring in the 2B system are secondary reactions involving hexone or organic impurities. The principal chemical variable in the operation of this column is the concentration of the nitric acid, most of which comes from the 2A Column. The higher the acid concentration, the greater is the difficulty of stripping the plutonium because nitric acid increases plutonium distribution into hexone. The 2B operation is therefore closely allied with that of the 2A Column, and an appreciable increase in the acidity of the 2B system must be compensated for by increasing the L/V ratio.

The total mass transfer is small, and density and heat effects are therefore negligible.

11.3 Losses and decontamination

As noted above, Pu losses in the 2B organic raffinate are a function of the L/V ratio and the acidity of the system. The decontamination is two to three-fold, but is not of sufficient magnitude to be important.

12. Third Plutonium Decontamination Cycle

The utilization of the third Pu decontamination cycle is dependent on the effectiveness of the previous operations. If the third cycle is required, the only feed preparation necessary is the addition of aqueous aluminum nitrate to the 2BP stream in order to realize the necessary salting strength. Except for small differences in acidity and flow ratios, the cycle is then identical to the second and involves the use of the 3A and 3B Columns. Variables are as discussed for the second cycle. The final purity and disposition of the aqueous plutonium stream is discussed in Chapter VII.

DECLASSIFIED

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B. PROPERTIES OF PROCESS MATERIALS

1. Hexone

1.1 Introduction

Methyl isobutyl ketone (4-methyl-2-pentanone), commonly known as hexone, is a colorless, mobile liquid with a typically sweet, ketonic odor.(101) It is produced by the condensation of acetone to mesityl oxide with subsequent hydrogenation of the oxide to the ketone. Factors leading to the choice of hexone as the solvent in the Redox process are discussed in the preceding section.

1.2 Physical properties

The physical properties of methyl isobutyl ketone are presented in Table IV-3. The properties listed are those of fundamental interest and importance in the Redox process.

1.3 Chemical reactions

The chemical properties of hexone are illustrated below by a series of reactions charcteristic of aliphatic ketones.(14)

1.31 Oxidation:

With strong oxidizing agents such as chromic acid, hexone is oxidized to a mixture of acetic, isobutyric, and isovaleric acids, carbon dioxide and water:

$$(CH_3)_2CH.CH_2.CO.CH_3 + \tfrac{3}{2}O_2 \longrightarrow (CH_3)_2CH.COOH + CH_3.COOH$$

$$(CH_3)_2CH.CH_2.CO.CH_3 + 2O_2 \longrightarrow (CH_3)_2CH.CH_2.COOH + CO_2 + H_2O.$$

1.32 Condensation:

Hexone condenses with aldehydes to form unsaturated ketones:

$$(CH_3)_2CH.CH_2.CO.CH_3 + CH_3.CH_2.CH_2.CHO \longrightarrow (CH_3)_2CH.CH_2CO.CH = CH.CH_2.CH_2.CH_3.$$

Hexone condenses with itself in the presence of various catalysts:

$$2(CH_3)_2CH.CH_2.CO.CH_3 \xrightarrow[\text{or}\ HCl]{NaOH} (CH_3)_2CH.CH_2.\overset{\overset{CH_3}{|}}{C}=CH.CO.CH_2-\overset{\overset{CH_3}{|}}{CH}.$$

Hexone condenses with hydrazines to form hydrazones.

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1.33 Addition reactions:

Characteristic of carbonyl compounds, hexone adds sodium bisulfite at a rate of 12 per cent in one hour when one equivalent of sodium bisulfite is employed.

$$(CH_3)_2CHCH_2COCH_3 + NaHSO_3 \longrightarrow (CH_3)_2CHCH_2\underset{\underset{SO_3Na}{|}}{\overset{\overset{OH}{|}}{C}}CH_3 .$$

1.34 Reactions with nitric acid:

One of the important specific reactions of hexone in the Redox process is that with nitric acid.(191) The main reaction of hexone and nitric acid consists of an oxidation of the ketone to alpha-nitroso methyl isobutyl ketone with subsequent hydrolysis and oxidation to methyl isopropyl diketone and dinitroisobutane.

$$(CH_3)_2CH.CH_2.CO.CH_3 + HNO_2 \longrightarrow (CH_3)_2CH.CH(NO).CO.CH_3$$

alpha-nitroso methyl isobutyl ketone

$$(CH_3)_2CH.CH(NO).CO.CH_3 \xrightarrow[dil.H^+]{H_2O} (CH_3)_2CH.CO.CO.CH_3 + H_2NOH$$

methyl isopropyl diketone

$$(CH_3)_2CH.CH(NO).CO.CH_3 \xrightarrow[dil.HNO_3]{H_2O} (CH_3)_2CH.CH(NO_2)_2 + CH_3COOH + HNO_2 .$$

1,1-dinitroisobutane

After an indeterminate induction period, this reaction is initiated by nitrous acid, and becomes autocatalytic through side reactions which produce additional nitrous acid. The initial reaction appears to be first order with respect to nitrous acid and nearly independent of the nitric acid concentration. At room temperature, when the nitric acid concentration is below about 0.3 M, the nitrous acid, if present initially in concentrations of from 0.0001 M to 0.01 M, disappears with no further reaction. At nitric acid concentrations greater than 0.3 M and nitrous acid concentrations greater than 0.001 M, the nitrous acid decreases to a minimum and then increases to an equilibrium value of 0.001 M, from which point there is continuous destruction of hexone with a reaction rate of about 0.03 per minute. Raising the temperature from 25°C. to 40°C. more than doubles the reaction rate, and reduces the nitric acid concentration necessary for a self-sustaining reaction to 0.2 M as compared to 0.3 M at 25°C.

Since the hexone-nitric acid reaction is exothermic, and since the reaction rates increase rapidly with temperature, under conditions of high nitric acid concentration (over 3 M) and poor heat transfer the reaction mixture becomes violently unstable. Reducing agents such as iron, which react with nitric acid to produce nitrous acid, accelerate the reaction, but sulfamate ion, ammonium ion, and dichromate ion, destroy nitrous acid and thus inhibit the hexone-nitric acid reaction.

Uranyl nitrate also destroys nitrous acid, through a complex photochemical reaction.(191)

Although nitric acid is added directly to the organic streams, the above reaction does not occur in the absence of nitrite ion and nitrous acid, and any nitrite ion which may be introduced as a contaminant of the process chemicals is quickly destroyed by one or more of the aforementioned reactions.

An additional safety factor is provided by the automatic proportioning pumps which are employed wherever nitric acid is added to hexone. These pumps maintain the flow of nitric acid at a rate which precludes dangerous admixtures, i.e., concentrated nitric acid plus an equal or smaller volume of hexone. The temperature of the hexone is measured before and after the addition of the nitric acid, by a recorder which activates an alarm in the event of a too-rapid increase in the temperature differential. Continuous scrubbing and distillation of the hexone in the Solvent Recovery operation prevents the build-up of any impurities which might contribute to this undesirable reaction.

Hexone does not react with aqueous solutions of aluminum nitrate nonahydrate under ordinary conditions. At elevated temperatures, (90°C.) however, the reaction proceeds similarly to that with nitric acid, presumably due to nitrous acid produced by hydrolysis of the aluminum nitrate.(160a)

1.4 Effect of irradiation

Exposure of hexone to process-level radiation (8×10^9 co./min./l. gross γ , 2×10^{12} co./min./l. gross β , measured at 10% geometry and 26 mg./l.Pu.) for more than 430 times (70 hours) the estimated contact time in the process results in no decomposition of the hexone, as indicated by the absence of gas evolution and of any change in disengaging times, (see under B9, below) and uranium, plutonium and fission product distribution ratios.(136) Hexone has also been found to be stable under exposures up to 1000 times the radiation level of Redox process streams.(93) Hexone subjected to the solvent recovery process after having been exposed to radiation is comparable in process performance to fresh, pretreated hexone.(136)

2. Hexone-Water Systems

2.1 Mutual solubilities

The solubilities of hexone in water and water in hexone are shown, as a function of temperature, in Figure IV-4. The solubility of hexone in water passes through a minimum of 1.41 weight per cent at 55°C.(146) The solubility of hexone in multisolute aqueous solutions varies markedly from that in pure water, and may be determined by use of the equation and coefficients given in Table IV-22.(166)

2.2 Mutual heats of solution

The heat of solution of water in hexone is 1,800 calories per mole

of water, while that of hexone in water is -2,250 calories per mole of hexone, both measured from zero to saturation at 25°C.(160)

2.3 Liquid-vapor equilibrium data

Liquid-vapor equilibrium data for the hexone-water systems are presented in Table IV-5A in the form of liquid and vapor phase compositions and relative volatilities for the temperature range from 88 to 114°C.(151) The boiling temperatures and vapor phase compositions of the hexone-water azeotrope for a series of pressures from 27 to 760 mm. of Hg are given in Table IV-5B.(14,147,151)

2.4 Miscellaneous properties

The density of water-saturated hexone at 25°C. is 0.7992 grams per cubic centimeter. The change in density with temperature is given under 3.4, below.

The viscosity of water-saturated hexone at 25°C. is 0.570 centipoises.(155) The change in viscosity with temperature may be computed from the equation under 3.4, below.

The interfacial tension between water-saturated hexone and water is 10.9 dynes per centimeter at 22°C.(114)

3. Other Solutions in Hexone

3.1 Uranyl nitrate in hexone

Uranyl nitrate is soluble in hexone to the extent of 113 ± 6 grams per 100 grams of hexone at 25°C.(201) Uranyl nitrate has been shown to carry between 3 and 4 molecules of water of hydration into hexone.(21)

A mixed phase crystal with the empirical formula $UO_2(NO_3)_2 \cdot 2.71\ H_2O \cdot 0.28$ hexone has been isolated. However, uranyl nitrate is not as tightly complexed in hexone as it is in tributyl phosphate, with the result that no definite formula can be assigned to the solvate, and no rate constants can be calculated for complex formation. Since stagewise calculations based on the trihydrate in hexone yield a more nearly straight operating line, the trihydrate is used for these calculations.

The density of solutions of uranyl nitrate in hexone may be computed by means of the equation given in Subsection 3.4 below. The apparent molar volume of $UO_2(NO_3)_2$ in hexone is about 65 cubic centimeters per gram mole.(155)

The viscosity of water-saturated solutions of uranyl nitrate in hexone may be calculated by means of the equations given in Subsection 3.4. The change in viscosity with temperature is given by another equation under 3.4, below.

The conductivity of solutions of uranyl nitrate in hexone is shown in Figure IV-6.(204) The equivalent conductance decreases with an increase in the concentration of uranyl nitrate.

The specific heat of solutions of uranyl nitrate in water-saturated hexone is shown as a function of the concentration of $UO_2(NO_3)_2$, in Figure IV-7. As shown in the figure, the specific heat decreases from 0.526 to 0.475 calories per gram of solution as the uranyl nitrate concentration is increased from 0 to 0.62 M.(157)

3.2 Nitric acid in hexone

The solubility relationships of the system nitric acid-water-hexone are presented in the ternary phase diagram, Figure IV-8.(61) The following are some typical saturated organic and aqueous phases in equilibrium with each other, as read from this diagram:

Organic Phase		Aqueous Phase	
Wt.% HNO_3	Wt.% H_2O	Wt.% HNO_3	Wt.% Hexone
0	2	0	2
2	2	8	2
8	2.5	16	2
20	10	30	2.5

The density of nitric acid solutions in hexone increases linearly with nitric acid concentration, as shown in Figure IV-9.(61,155) The apparent molar volume of nitric acid in hexone is about 30 cubic centimeters per gram mole.(155)

The viscosity of nitric acid solutions in hexone may be calculated from the equation given in Subsection 3.4.(155)

The conductivity of solutions of nitric acid in hexone exhibits a minimum at about 0.03 M. Equivalent conductance is shown in Figure IV-6 as a function of the nitric acid concentration. The ionization constant for nitric acid in hexone containing 1.23 weight per cent water, has been calculated to be about 2.5×10^{-7}.(97)

The specific heat of nitric acid solutions in hexone increases almost linearly with nitric acid concentration as shown in Figure IV-7.(157)

3.3 Miscellaneous solutes in hexone

Aluminum nitrate is soluble in water-saturated hexone to the extent of about 10^{-3} grams per liter.(161)

Chromic ion, Cr(III), has almost no measurable solubility in hexone (approximately 2×10^{-6} M). Its solubility is not appreciably affected by the salting strength of the system or the acidity of the organic phase.(102) Dichromate ion, however, is very soluble as evidenced by the distribution ratios cited in Subsection C6.

Ferrous and ferric nitrates are very sparingly soluble in hexone as indicated by the distribution ratio data presented in Subsection C6. (No direct measurement of the solubilities was found reported in the literature.)

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Sulfamic acid is soluble to the extent of 0.34 grams per liter of water-saturated (pretreated) hexone, at 26°C.

3.4 Mixed solutes in hexone

The density of water-saturated hexone solutions at 25°C. is given by the following equation:(158)

$$d_{25} = 0.7992 + 0.3500\ \underline{M}_{UN} + 0.0439\ \underline{M}_{HNO_3},$$

and may be computed at any desired temperature, t°C., by means of an additional equation:(155)

$$d_t = 0.9661\ d_{25} - 0.002029\ t + 0.001358\ t\ d_{25} + 0.0507.$$

These equations are valid in the following ranges:

$UO_2(NO_3)_2 \cdot 6H_2O$, 0 to 1.4 $\underline{M}$;

HNO_3, 0 to 1.0 $\underline{M}$.

The viscosity, η , in millipoises, of water-saturated hexone solutions at 25°C. may be obtained by:(155)

$$\log_{10}\eta = 0.7558 + 0.6433\ \underline{M}_{UN} + 0.0543\ \underline{M}_{UN}^2 + 0.1550\ \underline{M}_{HNO_3}.$$

The change in viscosity with temperature is given by:(155)

$$\frac{d(\log_{10}\eta)}{d(1/T)} = 434.3 + 360.5\ \underline{M}_{UN} + 2.02\ \underline{M}_{UN}^2 + 100\ \underline{M}_{HNO_3},$$

where $\underline{M}$ represents the concentration in moles per liter, and T is the absolute temperature in degrees Kelvin.

The refractive index, n_D^{25} , of solutions of uranyl nitrate and nitric acid in water-saturated hexone may be approximated by the equation:(208)

$$n_D^{25} = 1.3932 + (0.0017 - 0.0013\ \underline{M}_{UN})\ \underline{M}_{HNO_3} + 0.028\ \underline{M}_{UN}.$$

The minor constituents, iron, aluminum, and chromium, are so relatively insoluble that they do not significantly affect the properties of the organic solutions.

3.5 Impurities in hexone

The principal impurities found in hexone as received from the manufacturer are methyl isobutyl carbinol (MIBC), mesityl oxide (MO), and water. The purchase specifications for hexone are given below:

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157

Hexone Specifications(191a)

Refractive index, n_D^{20}	1.3953 ± 0.004
Color, ASTM D268-49	Maximum 15 Hazen standard
Acidity	0.05% as acetic acid
Distillation range, ASTM D286-46	Below 114°C., none
	Above 117°C., none
Purity	99.0% by volume
Impurities: Methyl isobutyl carbinol	0.6% by volume
Mesityl oxide	0.3% by volume
Oxidizing impurity	0.001 normal

Methyl isobutyl carbinol, $(CH_3)_2CHCH_2CHOHCH_3$, (abbreviated MIBC), is found in raw hexone in concentrations of from 0.2 to 0.6 weight per cent. (It is introduced into the hexone in its manufacture from acetone, by partial over-reduction of the intermediately formed mesityl oxide.) MIBC has an effect on decontamination which varies with the acidity of the aqueous phase. Under conditions of the ANL (acid) Flowsheet, MIBC in the presence of dichromate ion has a deleterious effect on Zr decontamination as shown under C4.55. Under acid-deficient conditions such as prevail in the ORNL No. 1 Flowsheet, Zr decontamination is not sensitive to MIBC concentration.(99) Furthermore, MIBC is readily oxidized to hexone, and is thus effectively removed by pretreatment. It is maintained below the specified limit of 0.05 weight per cent by the Solvent Recovery process.(138) (See Chapter IX for a description of this process.)

Mesityl oxide $(CH_3)_2CH = CHCOCH_3$ (abbreviated MO), is present in untreated hexone in amounts ranging from 0.2 to 0.7 weight per cent.(101) (MO is an intermediate product in the manufacture of hexone from acetone.) It has been shown to exert no significant effect on decontamination factors when present in concentrations of less than 1.0 weight per cent.(99,152,156) When present in concentrations of from 1.0 to 3.0 weight per cent in the hexone phase, it slightly increases the distribution of ruthenium into the aqueous phase.(156)

Mesityl oxide decreases plutonium extraction due to its effect on the stability of plutonium (VI). When it is present in concentrations of 0.02 per cent or greater, it reduces plutonium (VI) (probably to plutonium (V)) with a half-time of one half to one hour. A further reduction to plutonium (IV) and/or plutonium (III) occurs with half-time of several hours.(99) Mesityl oxide is effectively removed by pretreatment.

The impurities which might be formed in the oxidation of hexone by nitric and nitrous acids are methyl isopropyl diketone, 1, 1-dinitroisobutane, and isobutyric, acetic, and other organic acids. These products, if allowed to accumulate in the extractant, would affect column performance adversely and are therefore removed in the Solvent Recovery process.

The diketone has no effect on the distribution of plutonium or zirconium,(147,174) but in the presence of plutonium (IV) it decomposes to form oxalate ion, causing precipitation of plutonium (IV) oxalate in

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the 2BP and 3BP streams.(181,183) The formation of the precipitate is favored by heating, and any attempt to heat IBP, 2BP, or 3BP Redox streams should be preceded by the removal of 90-95 per cent of the dissolved organic compounds.(183) The diketone is quantitatively removed by the caustic wash in the Solvent Recovery process.(147)

The 1, 1-dinitroisobutane appears to have no effect on column performance, and is effectively removed in the Solvent Recovery process as are the organic acids.

4. Aqueous Aluminum Nitrate Solutions

4.01 Introduction

Aluminum nitrate is employed as a salting-out agent in the Redox process. It is a highly water-soluble salt of high ionic strength and, consequently, is efficient in effecting the distribution of uranium and plutonium from the aqueous to the hexone phase.

The aqueous $Al(NO_3)_3$ systems covered hereunder include those containing HNO_3 and $NaNO_3$ as additional components, and also those containing $Na_2Cr_2O_7$, $Fe(NH_2SO_3)_2$, and hexone where data are available. Aqueous $Al(NO_3)_3$ solutions which also contain $UO_2(NO_3)_2$ are treated in Subsection B5.

4.02 Solubility

The solubility of $Al(NO_3)_3$ in water is given in Figure IV-10 as the zero HNO_3 parameter. A saturated solution at 25°C. contains 43 weight per cent $Al(NO_3)_3$(12), or 2.8 moles per liter based on a density of 1.37 g./ml.(10)

The addition of HNO_3 to the system markedly decreases the solubility of $Al(NO_3)_3$ as shown in Figure IV-10 and Figure IV-11. The latter plots show also the decreased solubility of $Al(NO_3)_3$ in HNO_3 with decrease in temperature.

An approximation to the solubility of $Al(NO_3)_3$ in aqueous solutions of $NaNO_3$ at 20°C. is given by the linear equation: $Y = 42.5 - X$, where Y is the weight per cent of anhydrous $Al(NO_3)_3$ in the solution and X is the weight per cent of $NaNO_3$.

The solubility of $Al(NO_3)_3$ in multicomponent systems is given in Figure IV-12 as a function of temperature for both neutralized and unneutralized composite aqueous Redox wastes (Flowsheets ORNL and HW No. 4).(196) For a discussion of the properties of $Al(NO_3)_3$ in the waste neutralization and disposal phases of the Redox process see Chapter X.

4.03 Density

The densities of aqueous process streams are used throughout the Redox process for numerous purposes, which include: (a) feed make-up analysis; (b) control of process stream compositions; (c) control of column

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performance, flooding, etc., and (d) calculation of H.E.T.S. and H.T.U. values.

The densities of aluminum nitrate solutions at 18°C. are given in Figure IV-13. Molarity-weight per cent conversion may be read from the graph or obtained from the general relationship: weight per cent = molarity x $\frac{\text{formula weight}}{10 \times \text{density}}$, where the molarity and density (in grams per cu.cm.) are taken at the same temperature. A nomograph relating temperature, molarity, and specific gravity of aluminum nitrate solutions is shown in Figure IV-14A.(134)

The densities of aluminum nitrate solutions at several nitric acid concentrations are included in Figure IV-15.(155)

Densities for multicomponent systems may be calculated from the equations which with their coefficients of temperature and molarity, are presented in Table IV-16. Included are such minor components as $Na_2Cr_2O_7$ and hexone.(155)

4.04 Viscosity

The viscosities of process solutions greatly affect column performance through the influence of viscosity on diffusion, velocity of the dispersed phase, droplet size and the settling rate of entrained drops of the continuous phase.

Viscosity data are best expressed by equations. The equations and their molar and temperature coefficients are given in Table IV-16 for a multicomponent system.(155)

4.05 Hydrogen ion concentration, pH

Due to hydrolysis, stoichiometrically neutral aqueous $Al(NO_3)_3$ solutions give an acidic reaction. The pH varies from 1.4 for a 1.0 M solution to 0.1 for a 2.4 M solution. Since fission-product decontamination in the IA Column is improved by the use of IAS solution with a higher pH than that of an untreated aluminum nitrate solution, the IAS solution is made 0.2 M acid deficient by the addition of NaOH.

The pH of $Al(NO_3)_3$ solutions of various concentrations, as a function of added acid or base is shown in Figure IV-17. A nomograph relating pH, $Al(NO_3)_3$ molarity, and HNO_3 molarity, is given in Figure IV-14B.(134)

The addition of one or two moles per liter of $NaNO_3$ has little effect on the pH of acid solutions of aluminum nitrate or uranyl nitrate, but acid-deficient solutions of aluminum nitrate show about 0.17 pH unit drop per mole of $NaNO_3$.(172)

4.06 Saturation temperatures

The saturation temperatures of aqueous solutions of $Al(NO_3)_3$ and HNO_3 have been determined by both the freezing point (first appearance of solid phase) and the melting point (last evidence of solid phase).

Temperature-composition phase diagrams for the $Al(NO_3)_3$ - H_2O and $Al(NO_3)_3$ - HNO_3 - H_2O systems are plotted in Figure IV-10 and Figure IV-18.(12,149) Extrapolation of the melting point isotherms of Figure IV-19 to zero concentration of $UO_2(NO_3)_2$ yields the following data for the $Al(NO_3)_3$ - HNO_3 - H_2O system: (149)

Melting Point, $Al(NO_3)_3$ - HNO_3 - H_2O System

HNO_3 Concentration	$Al(NO_3)_3$ Molarity					
	At -5°C.	At -10°C.	At -15°C.	At -20°C.	At -25°C.	At -30°C.
0.0 M	0.66	1.4	1.32	1.57	1.73	--
0.15 M	0.57	0.95	1.28	1.44	1.62	--
0.30 M	0.52	0.90	1.175	1.36	1.51	1.66
0.60 M	0.35	0.76	1.04	1.25	1.47	1.57

Freezing-point data for neutralized and un-neutralized composite Redox wastes are included in Figure IV-12. These data cover the ranges 0.8 to 1.6 M $Al(NO_3)_3$ for neutralized waste, and 1.0 to 2.8 M $Al(NO_3)_3$ for un-neutralized waste.(196) Freezing points are not changed appreciably by the presence of process amounts of hexone or sodium dichromate.(149)

4.07 Boiling point

Boiling point and composition data from the batch evaporation of a stream initially 0.63 molar in both $Al(NO_3)_3$ and HNO_3 are given in Table IV-20. The data show that upon evaporation of 87 volume per cent of the original charge, the vapor temperature increases from 99.5 to 118°C. as the $Al(NO_3)_3$ and HNO_3 concentrations in the residue increase to 5.0 and 1.33 M, respectively.(140) The boiling points of composite Redox aqueous waste (HW No. 4 Flowsheet) at various $Al(NO_3)_3$ concentrations are given below:(196)

Un-neutralized		Neutralized	
$Al(NO_3)_3$ Concentration, M	Boiling Point, °C.	$Al(NO_3)_3$ Concentration, M	Boiling Point, °C.
2.532	114	1.328	107
2.667	115	1.462	109
2.800	116	1.620	110

4.08 Specific heat

The specific heats of aqueous $Al(NO_3)_3$ solutions are plotted along with those of $UO_2(NO_3)_2$ and HNO_3 solutions in Figure IV-21. The values are seen to decrease with increasing salt concentrations.

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4.09 Heats of solution

The heats of solution of $Al(NO_3)_3 \cdot 9H_2O$ at 25°C. in water and in 66 per cent HNO_3 are tabulated below. All heats are negative; i.e., heat is absorbed:(160)

Initial Composition		Final Composition		Heat of Solution
HNO_3, G./L.	$Al(NO_3)_3 \cdot 9H_2O$, G./L.	HNO_3, G./L.	$Al(NO_3)_3 \cdot 9H_2O$, G./L.	Cal./G. Mole of $Al(NO_3)_3$
923	0	917	16.5	-15,100
917	16.5	914.4	23.0	-11,700
0	0	0	6.6	- 7,200

4.10 Solubility of hexone in aqueous solutions

The solubility of hexone in aqueous solutions is depressed by the presence of $Al(NO_3)_3$, e.g., from 1.87 weight per cent hexone at 25°C. in water to 0.62 weight per cent in 2 M $Al(NO_3)_3$. These solubility data may be calculated at any desired temperature from 0 to 130°C. for any or all of the components in the system $UO_2(NO_3)_2$ - $Al(NO_3)_3$ - HNO_3 - H_2O, by means of the equation and temperature coefficients given in Table IV-22.(166)

4.11 Flash point

The flash point is defined as the temperature at which a solvent gives off sufficient vapor to produce a flammable vapor-air mixture capable of ignition by an open flame as determined by certain standard apparatus. The activity or vapor pressure of hexone over a hexone-saturated aqueous solution is sufficiently great to make the flaming characteristics not too different from hexone itself.

The flash point of any aqueous system containing hexone is dependent upon the temperature prevailing at the time of contact with the organic phase, the duration of storage of the aqueous system, and the conditions of storage, i.e., temperature and ventilation within the storage vessel. For example, effluent IAW (ANL Flowsheet, 1.3 weight per cent hexone) has a Tag closed-cup flash point of 96°F.(202) as compared to 60°C. for hexone itself. However, IAW stored at 25°C. for six weeks in a closed vessel has been found to exhibit a flash point of over 170°F.(202) This high figure is attributed to decomposition of the hexone in the acid dichromate system.

5. Aqueous Uranium Nitrate Solutions

5.01 Introduction

The properties of aqueous uranium solutions play an important part in the Redox process throughout the feed preparation step, the IA Column extraction, and the subsequent uranium decontamination cycles. Presented in this subsection are data concerning aqueous uranyl nitrate systems, including those also containing HNO_3, $Al(NO_3)_3$, $NaNO_3$, $Na_2Cr_2O_7$, $Fe(NH_2SO_3)_2$, and hexone.

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5.02 Solubility

A saturated solution of uranyl nitrate at 25°C. contains about 72 per cent by weight of $UO_2(NO_3)_2 \cdot 6H_2O$(13) or 2.6 moles per liter. The temperature-solubility phase diagram for the $UO_2(NO_3)_2$ - H_2O system is presented in Figure IV-23.(48)

The presence of nitric acid markedly reduces this solubility as shown by the temperature-composition phase diagram for the $UO_2(NO_3)_2$ - HNO_3 - H_2O system given in Figure IV-24.(144) A solution of 60 per cent nitric acid saturated with respect to uranyl nitrate contains only 23.5 per cent $UO_2(NO_3)_2$ by weight at 25°C. Additional solubility data are included with the freezing point data under 5.06, below.

5.03 Density

The densities of aqueous streams containing uranyl nitrate are required in feed make-up and control of column performance (IA Column and subsequent uranium decontamination cycles). Density differences between phases in a two-phase system directly affect droplet size and flooding capacity, and therefore afford a convenient measure of overall performance.

A large density gradient exists in both phases in the IA extraction section, whereas the scrub section shows little change in density with stage number. Table IV-25 shows the stagewise change in aqueous density in both the IA and IC Columns as determined by laboratory countercurrent batch equilibrations. These density profiles are given for the ANL June 1948, ORNL June 1949, and HW No. 4 Flowsheets in the IA Column and for the ANL June 1948 Flowsheet in the IC Column.

The densities of the system $UO_2(NO_3)_2$ - $Al(NO_3)_3$ - HNO_3 - H_2O are plotted in Figure IV-15. The values are seen to increase linearly with $Al(NO_3)_3$ at the low concentrations specified.(155)

The molar and temperature coefficients of equations from which densities may be computed for any solution in a multicomponent system are given in Table IV-16. These include such minor components as $Na_2Cr_2O_7$, $Fe(NH_2SO_3)_2$, and hexone.(155)

Densities at 100°C. for the system $UO_2(NO_3)_2$ - HNO_3 - H_2O are shown in Figure IV-26. Also included are temperature coefficients necessary to convert the density at 100°C. to the density at any other temperature.(48)

5.04 Viscosity

Viscosity data are required for the correlation of column performance and process flows with aqueous stream compositions (cf. 4.04, above). The desired data for any combination of constituents in a multicomponent system may be obtained by means of the viscosity equations presented in Table IV-16.

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5.05 Hydrogen ion concentration, pH

The apparent acidity of aqueous solutions of aluminum nitrate and uranyl nitrate increases with an increase of salt concentration due to hydrolysis. The decrease in pH is illustrated in Figure IV-27 for the system $UO_2(NO_3)_2$ - $Al(NO_3)_3$ - HNO_3 (or NaOH) - H_2O.

Sodium nitrate causes a slight lowering of pH in acid-deficient or neutral solutions, but produces no effect in acid solutions, while $Na_2Cr_2O_7$ in concentrations up to 0.05 M does not appreciably affect pH.(172)

5.06 Saturation temperature

The temperature-composition phase diagrem for the $UO_2(NO_3)_2$ - H_2O system is shown in Figure IV-23.(48)

The system $UO_2(NO_3)_2$ - HNO_3 -H_2O is presented in a similar fashion in Figure IV-24.(144)

The melting points of the system $UO_2(NO_3)_2$ - $Al(NO_3)_3$ - HNO_3 - H_2O are plotted in Figure IV-18, and the melting point isotherms for this same system are shown in Figure IV-19.(149)

5.07 Boiling point

The boiling points of the $UO_2(NO_3)_2$ - H_2O system are included in Figure IV-23.(48) The boiling points for the $UO_2(NO_3)_2$ - HNO_3 - H_2O system in the 0 to 80 weight per cent $UO_2(NO_3)_2$ and 0 to 60 weight per cent HNO_3 ranges are shown in Figure IV-26.(48)

5.08 Specific heat

The specific heat of uranyl nitrate solutions is plotted as a function of concentration in Figure IV-21, in conjunction with the $Al(NO_3)_3$ and HNO_3 curves. The specific heat varies inversely with solute concentration in all three instances.

5.09 Solubility of hexone

The solubility of hexone in the aqueous system $UO_2(NO_3)_2$ - $Al(NO_3)_3$ - HNO_3 or any combination of these constituents may be obtained from the equation in Table IV-22. The data, covering the temperature range from 0 to 130°C., show that uranyl nitrate decreases the solubility while nitric acid increases the solubility of hexone in the aqueous phase.

5.10 Refractive index

The refractive indices of uranyl nitrate solutions are plotted in Figure IV-28.

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5.11 Miscellaneous

The following four physical properties of aqueous uranyl nitrate solutions are given in Table IV-29: (a) heat of solution, (b) diffusion coefficient, (c) partial pressure of aqueous solutions, (d) freezing point lowering of aqueous solutions.

The conversion of concentration units is conveniently handled by the use of the general equation: weight per cent = molarity x (formula weight)/(10 x density), where the density (in grams per cu.cm.) and molarity are taken at the same temperature.

6. Aqueous Plutonium Nitrate Solutions

6.01 Introduction

The physical properties of aqueous plutonium solutions can be considered of interest in the Redox process only at the final plutonium product concentration step, since the plutonium concentration in other process solutions is too low to exert an appreciable influence on the physical properties of the system. The effect of process amounts of Pu in 2BP or 3BP, even after the concentration step, upon such properties as density, freezing point, and viscosity, is slight. (See also Chapter VII.) On the other hand, the chemical behavior of plutonium in solution is of fundamental importance throughout the entire process. Both types of data are included in this subsection.

6.02 Solubility

The nitrates of plutonium are considered very soluble in water. However, saturated plutonium nitrate solutions require the presence of 1 to 5 moles of nitric acid per liter to prevent hydrolysis and subsequent polymerization or precipitation of the hydroxide. (See 6.08 concerning dilute Pu solutions.)

The solubility of Pu(IV) nitrate is in the range of 2.1 to 2.5 moles per liter at 25°C., in the presence of ca. 1.8 M nitric acid.(51,59) The approximate solubility of Pu(VI) nitrate is 2.1 moles per liter at 25°C.(50,51)

6.03 Density

The densities of Pu(IV) nitrate - nitric acid solutions are given below as a function of solution composition: (46)

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$Pu(NO_3)_4$ Concentration, M	Weight %	HNO_3 Concentration, M*	Density, G./Cu.Cm.
0.24	10	2.9	1.14
0.28	11	3.2	1.16
0.34	13	4.2	1.20
0.42	16	5.5	1.26
0.59	21	6.1	1.32
0.92	30	10.3	1.52
1.67	45	14.0	1.82
2.59	66	12.0	1.93
3.35	78	11.0	2.08
3.60	82	12.0	2.15

*)Estimated from the density equation of Table IV-16 by adding a $Pu(NO_3)_4$ term with a molar coefficient of 0.22. This coefficient is derived from data showing a solution containing 2.5 M Pu(IV) nitrate and 1.7 M HNO_3 to have a specific gravity of 1.6(59)

6.04 Saturation temperatures

The freezing and melting points of Pu(IV) nitrate solutions are given below:(17)

$Pu(NO_3)_4$ Concentration, M	Weight %	HNO_3 Concentration, M*	Freezing Point, °C.	Melting Point, °C.	Density, G./Cu.Cm.(25°C.)
0.76	24	12.3	-62	-28	1.55
1.0	30	13.2	-63	-44	1.63
1.6	42	15.2	-70	-53	1.82
--	49	--	-79	-57	

*) Estimated as in the table under 6.03 above.

The freezing temperature is given as the point of first evidence of the formation of a solid phase, and the melting temperature as the point of first evidence of the formation of a liquid phase. The wide spread between the freezing points and melting points in the table above is probably due to super-saturation of the solute in the freezing-point determinations.

6.05 Ionic species

All of the plutonium valence states possible in aqueous solutions are encountered in Redox process streams: Pu (III), blue-violet in color; Pu (IV), green (the polymeric form of Pu (IV) stable at pH's above 1.0 to 1.3 is brown; see Subsection 6.08 below); Pu (V), colorless; and Pu (VI), pink-orange. The ionic species present in a non-complexing medium are Pu^{+3}, Pu^{+4}, PuO_2^{+}, and PuO_2^{+2}, all highly hydrated.(78) Pu^{+4} and PuO_2^{+2}, however, are complexed by nitrate ion. In 2 M acid the equilibrium constant for the reaction, $Pu^{+4} + NO_3^{-} \rightleftharpoons Pu(NO_3)^{+3}$, is ca. 2.9.(74)

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Nitrate ion, therefore, is an effective salting agent for Pu (IV), since it is probable that Pu (IV) extracts as the nitrate complex or the neutral molecule. The equilibrium constant for the reaction $PuO_2^{+2} + NO_3^- \rightleftharpoons PuO_2NO_3^+$, is ca. 0.19 at 8 M nitrate ion concentration.(118)

Pu (IV) is highly susceptible to complex formation with sulfate ion, the equilibrium constant for the reaction, $Pu^{+4} + HSO_4^- \rightleftharpoons PuSO_4^{+2} + H^+$, being ca. 500 at 2.3 molar acid concentration.(75) The distribution of this sulfate complex in the 2A Column (HW No.4 Flowsheet, 0.1 M sulfate ion in the 2AF) in the absence of high concentrations of $Al(NO_3)_3$ salting agent would normally favor the aqueous phase, increasing Pu waste losses in the 2AW. However, process amounts of ferric ion preferentially complex the sulfate and minimize the difficulty.(42)

6.06 Oxidation - reduction couples

The formal oxidation potentials of the Pu series, defined as the potentials at which the concentration of oxidized and reduced species are equal, are given below:(66)

Couple	pH	Reaction	Oxidation Potential at 25°C., Volts (Referred to the $H_2 \rightarrow 2H^+$ Couple As Zero)
1. V - VI	0-5	$PuO_2^+ \rightarrow PuO_2^{+2} + e^-$	-0.93
2. III - IV	0-1.4	$Pu^{+3} \rightarrow Pu^{+4} + e^-$	-0.96
3. IV - V	1.4-8	$Pu^{+4} + 2H_2O \rightarrow PuO_2^+ + 4H^+ + e^-$	-1.004
4. III - VI	0	$Pu^{+3} + 2H_2O \rightarrow PuO_2^{+2} + 4H^+ + 3e^-$	-1.015
5. IV - VI	0	$Pu^{+4} + 2H_2O \rightarrow PuO_2^{+2} + 4H^+ + 2e^-$	-1.048

Writing the equations with the number of electrons involved on the right, the sign convention is used whereby the oxidized form of any couple will oxidize the reduced form of any couple of algebraically greater potential. Conversely, the reduced form of any couple will reduce the oxidized form of any couple of lower oxidation potential.

Comparing the above Pu couples with the dichromate oxidation potential: $2Cr^{+3} + 7H_2O \rightarrow Cr_2O_7^= + 14H^+ + 6e^-$; $E^o = -1.36$; it is seen that $Cr_2O_7^=$ is thermodynamically capable of oxidizing the reduced form of any of the Pu couples listed. The ferrous-ferric couple: $Fe^{+2} \rightarrow Fe^{+3} + e^-$; $E^o = -0.771$, shows that Fe^{+2} will reduce the oxidized form of any of the Pu couples listed.

6.07 Disproportionation

The most important disproportionation mechanism of Pu is the following: $2Pu^{+4} + 2H_2O \rightleftharpoons Pu^{+3} + PuO_2^+ + 4H^+$. This slow disproportionation,

followed by the more rapid reaction: $PuO_2^+ + Pu^{+4} \rightleftharpoons PuO_2^{+2} + Pu^{+3}$, is the mechanism for the oxidation of Pu (IV) to Pu (VI) at macro concentrations of plutonium, the role of the oxidizing agent being to convert the Pu (III) formed to Pu (IV).

In the reduction of Pu (VI) to Pu (III) the above disproportionation mechanism is reversed: $PuO_2^+ + Pu^{+3} + 4H^+ \rightleftharpoons 2Pu^{+4} + 2H_2O$, the role of the reducing agent being to reduce PuO_2^{+2} to PuO_2^+ and Pu^{+4} to Pu^{+3}.

Due to the numerical similarity of the oxidation potentials of Pu listed in 6.06, above, and to the rapid equilibrium of the electron transfer reaction: $Pu^{+4} + PuO_2^+ \rightleftharpoons PuO_2^{+2} + Pu^{+3}$ it is possible for all Pu species to co-exist in aqueous solution; e.g., a solution of pure Pu (IV) salt in 0.5 M HCl contains at equilibrium at 25°C., 27.2% Pu (III), 58.4% Pu (IV), 13.6% Pu (VI), and 0.8% Pu (V).(77)

6.08 Plutonium (IV) polymer

When the acidity of a Pu (IV) solution falls to about 0.01 molar, a polymeric species of Pu (IV) is formed in a matter of minutes.(68) This material is a polymeric hydroxide containing approximately four hydroxyls per plutonium ion.(65) At an acidity of ca. 0.1 molar, this polymer can be formed at elevated temperatures, but the reaction is slow.(68) Between pH 2.5 and 3, precipitation of the polymer occurs.(65)

The Pu (IV) polymer is a positive colloid which is electrostatically adsorbed on substances such as paper, sand, and glass, which assume negative surface charges when immersed in water.(72) The conversion of the colloid into the nitrate complex occurs slowly in 1 M HNO_3, the rate increasing with increasing acid concentration and decreasing if the polymeric solution has been previously heated. Depolymerization is very rapid at high temperatures in concentrated HNO_3.(72) The oxidation of the Pu (IV) polymer to Pu (VI) by dichromate is slow even at 85°C.(118)

Polymeric Pu (IV) may be formed in acid-deficient dissolver solution in any flowsheet and in various process streams in an acid-deficient flowsheet. An ionic Pu (IV) solution, however, is stable for about 1 day in a solution 1.92 M $UO_2(NO_3)_2$, 0.20 M acid-deficient, contrasting with the observed very rapid polymerization in acid-deficient aluminum nitrate solutions.(92) When the IA Column is operated under acid-deficient flowsheet conditions, the plutonium must first be oxidized to Pu (VI) and maintained as such by excess oxidant in order to avoid the formation of inextractable Pu (IV) polymer. In acid columns, such as the 2A Column, Pu (IV) remains unpolymerized.

6.09 Precipitation of plutonium

When aqueous plutonium streams, saturated with hexone, are heated to 80°C., or above, oxalate ion is formed from the methyl isopropyl diketone present as a hexone impurity or decomposition product, and precipitates

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the plutonium (IV) as the oxalate. Thus, for those Redox streams which are heated, a simple stripping operation removing 95 per cent of the hexone, is a prerequisite.(183)

6.10 Photoreduction and radiation stability of Pu (VI)

The autoreduction and photoreduction of Pu (VI) produce Pu (IV), an oxidation state which results in high Pu waste losses if present in IA Column operation (see 6.08 and 6.12).

In the absence of dichromate, the rate (at 25°C.) of Pu (VI) reduction by the products of its own alpha particle bombardment of the aqueous solution is 0.2 to 0.3 per cent per day of the total Pu present.(62) No reduction is apparent upon 1 hour's exposure to the beta and gamma radiation of dissolver solution containing 5 curies per liter gross beta radioactivity.(118)

Photoreduction of Pu(VI) to Pu(IV) takes place upon the absorption of light from the blue regions of the visible spectrum. The extent and rate of reduction are dependent upon light intensity, temperature, acidity, plutonium concentration, and uranium concentration. The reduction takes place to a measurable extent only in the presence of hexone.(208) When an aqueous uranyl nitrate-nitric acid solution containing originally 0.14 grams of Pu(VI) per liter, 0.10 M $Na_2Cr_2O_7$, and 1.3 M $Al(NO_3)_3$, is equilibrated with hexone to give an aqueous phase of 0.115 M $UO_2(NO_3)_2$ and ~0.16 M HNO_3 at 25°C., the Pu(IV) concentration increases at the rate of about 10 per cent per hour under fluorescent light intensity of 30 to 40 foot-candles.(198) The increase of Pu (IV) is approximately linear for the first few hours and varies inversely with uranium concentration.

6.11 Gas evolution

In macro concentrations of plutonium, the intense alpha particle bombardment to which the water of the solution is subjected, causes some decomposition of the water into gaseous products.(153) The mechanism for this phenomenon probably involves (a) stripping of an electron from a water molecule by the alpha particle and (b) reaction of this positively charged water molecule with a neutral water molecule to form hydrogen peroxide and free hydrogen. The peroxide reacts with any oxidizable or reducible material present or decomposes, liberating oxygen.

The pressure developed on storage of plutonium solutions is a function of free volume of the container. In a system of one milliliter free volume and three milliliters of solution of 250 grams of Pu per liter, the pressure developed is calculated to be 20 atmospheres in 1 year and 700 atmospheres after about 37 years (at which time all of the water is converted to hydrogen and oxygen). The corresponding pressures for 25 ml. of free space are 1.8 and 30 atmospheres, while for 1000 ml. of free space the pressures are 1.02 and 1.7 atmospheres. The above factors, high pressures and formation of explosive gas mixtures, necessitate the use of vented vessels for storage and handling of Pu solutions of high concentrations.(153)

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6.12 Chemistry of plutonium in dissolver solution

The predominant plutonium species in an acid solution of dissolved irradiated uranium slugs is Pu(IV).(118) In this valence state the distribution ratio, E_a^o, of Pu is too low to insure adequate recovery in the IA Column. An increase in pH, e.g., contact with acid-deficient aluminum nitrate scrub solution, causes rapid polymerization of the Pu(IV), which in IA Column operation results in high Pu waste losses to the IAW. Chiefly for the latter reason, the plutonium is oxidized to the (VI) state before entering the IA Column. This oxidation step is also necessary when filter aids such as Super Filtrol are employed as scavenging agents, for at pH's from 0.0 to 0.1, Pu(IV) is adsorbed almost completely on the filter aid and cannot be entirely removed, thus making a fission-product scavenging step impractical. On the other hand, Pu (VI) is only 10 per cent adsorbed on Filtrol, and can be more than 99 per cent removed by leaching with dilute nitric acid.(118)

The oxidation of plutonium in Redox dissolver solutions to Pu(VI), is best accomplished at elevated temperatures (85 - 100°C.) in the presence of ca. 0.1 M $Na_2Cr_2O_7$ and 0.1 M HNO_3.(118) There is evidence that un-complexed Pu(IV) is very rapidly oxidized under those conditions (50 per cent oxidized in one minute) but that a 2 to 4-hour period is necessary to convert the less readily oxidizable Pu (IV) species present in process solutions to Pu(VI).(118)

The rate of oxidation falls off rapidly with increasing HNO_3 concentration. (76,118) This effect may be attributed in part, to the stabilization of Pu(IV) by the formation of nitrate complexes or, if the mechanism of oxidation involves disproportionation of Pu(IV), to the decreased rate of the following disproportionation reaction at higher H^+ ion concentration according to the law of mass action: $2Pu^{+4} + 2H_2O \rightleftharpoons Pu^{+3} + PuO_2^+ + 4H^+$. This is followed by the reaction, $PuO_2^+ + Pu^{+4} \rightleftharpoons PuO_2^{+2} + Pu^{+3}$, and the oxidation of Pu(III) to Pu(IV).(92) In addition, assuming that $CrO_4^=$ is the ion responsible for the oxidation of Pu(IV), H^+ in all probability slows the reaction by suppressing the second ionization of chromic acid: $HCrO_4^- \rightleftharpoons H^+ + CrO_4^=$.

6.13 Reduction of Pu in the IB Column

The reduction of Pu(VI) to Pu(III) in the IB Column by ferrous ion is rapid, the reaction being complete in less than 15 seconds.(197) High concentration of Pu and low concentration of reducing agent favor the following mechanism: (a) direct reduction of PuO_2^{+2} to PuO_2^+ by Fe(II), followed by (b) the reaction, $PuO_2^+ + Pu^{+3} + 4H^+ \rightleftharpoons 2Pu^{+4} + 2H_2O$ (rate-determining step), followed by (c) direct reduction of Pu(IV) to Pu(III).(71,76) At low Pu concentrations (0.2 to 0.4 grams per liter) such as found in the IB Column, direct reduction of PuO_2^{+2} to Pu(III) is more probable. The oxidation of Pu(III) to Pu(IV), occurring due to nitrate ion, is slow at room temperature in dilute HNO_3, 0.2 M or less,(76) and is prevented by ferrous ion in the IB Column.

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6.14 Chemistry of plutonium in cross-over oxidation

The chemistry of the batch cross-over oxidation step for the conversion of Pu(III) to Pu(VI) between the 1B and 2A Columns is similar to the oxidation of dissolver solution. The reaction proceeds first by the very rapid oxidation of Pu(III) to Pu(IV) by dichromate ion in dilute nitric acid(76). The rate of reaction of the remaining step, the oxidation of Pu(IV) to Pu(VI), is a function of several variables: (a) the Pu(IV) species (whether uncomplexed Pu(IV), Pu(IV) nitrate complex, or Pu(IV) polymer), (b) Pu concentration, (c) temperature, and (d) nitric acid concentration. The rate and extent of oxidation of Pu(IV) are not materially affected by concentrations of $UO_2(NO_3)_2$ as high as 1.0 M, or by Cr(VI) concentration in the range 1.25 to 5.0 mg. Cr(VI) per milliliter. In Redox process solutions, which contain approximately 0.2 to 0.4 g.Pu per liter, the Pu(IV) - Pu(VI) oxidation reaction is slow at room temperatures with the half-times reported ranging from 7 hours for an ORNL pilot-plant IBP solution to 80 hours for a synthetic hexone-free IBP solution. The difference in reaction rates is attributed to the catalytic effect of corrosion products and hexone decomposition products present in the ORNL IBP solution. Reaction rates for the same conditions with trace quantities of Pu (0.1 to 2 μg./ml.) are faster, with half-times ranging from 80 minutes for a hexone-saturated IBP solution to 33 hours for a hexone-free synthetic solution.(185) At elevated temperatures (85 to 100°C.) with flowsheet concentrations of $Cr_2O_7^=$ and HNO_3 (0.02 and 0.1 M respectively) it is believed that the reaction will be complete within 2 to 4 hours. In an aqueous solution comparable to IBP, containing 8.5 M NH_4NO_3, 0.35 M HNO_3, 42,800 Pu(IV) counts per minute per milliliter, and 0.5 mg. Cr(VI) per milliliter, the Pu(IV) was 98 per cent oxidized to Pu(VI) in 10 minutes at 81°C.(78a) A half-time of approximately 1.5 minutes for the oxidation of trace quantities of Pu(IV) to Pu(VI) by $Cr_2O_7^=$ at 75°C. in an aqueous 1 M HNO_3 solution has also been reported.(76) The difference in rate between the (III)-(IV) and (III)-(VI) reactions is attributed to the fact that the (III)-(IV) reaction involves only the transfer of an electron and does not require the formation or breaking of oxygen bonds as is the case with the formation of PuO_2^{+2}.

The practically instantaneous reaction rate for the oxidation of Pu(III) to Pu(IV), which is complete in less than 20 seconds at 25°C.,(180) is utilized in the continuous cross-over oxidation, whereby the Pu(III) is converted to Pu(IV) by the acid and dichromate either in the IBP or 2AF Tank or in the 2A Column at the ambient temperature (see Section A). The 2A Column is maintained acidic to prevent the formation of the stable, difficultly extractable Pu(IV) polymer.

7. Sulfamic Acid

7.1 Introduction

Sulfamic acid, or rather the sulfamate ion, $NH_2SO_3^-$, is used in the Redox process as a holding reductant. The sulfamic acid is required in this role in all columns in which plutonium is separated from uranium by

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the selective reduction of plutonium to the hexone-insoluble Pu(III) state, i.e., in the 1B, 2D, and 3D Columns. This reduction is accomplished by ferrous ion, the role of the sulfamate ion being to prevent the premature oxidation of Fe(II) to Fe(III) by nitrite ion, and hence re-oxidation of Pu(III) to Pu(IV).

7.2 Physical properties

Formula	HSO_3NH_2
Molecular weight	97.09
Appearance	White crystalline solid, non-volatile, non-hygroscopic, odorless.(3)
Melting point	205°C., with decomposition.(3)
Solubility in hexone (water saturated, 24°C.)	0.35 g./l.

Solubility in water: (2, 3, 104)

Temperature, °C.	G. Sulfamic Acid/100 G. H_2O
0	14.68
10	18.56
20	21.32
25	21.80
30	26.09
40	29.49
50	32.82
60	37.10
70	41.91
80	47.08

In general, all ordinary salts of sulfamic acid are highly soluble in water, being in most instances more soluble than the corresponding nitrate or sulfate of that metal.

7.3 Chemical properties

7.31 Acid strength

Sulfamic acid is considered a strong acid, being less strong than nitric acid, but stronger than phosphoric acid.(3) Its pH, as a function of concentration, is as follows:

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Concentration of Sulfamic Acid, M	pH
1.0	0.41
0.75	0.50
0.50	0.63
0.25	0.87
0.10	1.18
0.05	1.41
0.01	2.02

7.32 Hydrolysis

Sulfamic acid hydrolizes according to the equation:(2, 104)

$$NH_2SO_3^- + H_2O \rightleftharpoons NH_4^+ + SO_4^=.$$

The hydrolysis rate at room temperature is slow-- about 0.1 per cent per day for either a 1 M sulfamic acid or 1 M sulfamic acid, 1 M HNO_3 solution. A similar rate is found for a 1.0 M sulfamic acid, 1.0 M $Al(NO_3)_3$, and 0.3 M HNO_3 solution. The hydrolysis is a first order reaction with rate constants at 80°C. of 0.0456 and 0.0825 per hour (i.e., 4.56 and 8.25% decomposed per hour) for 1 and 10 per cent solutions, respectively.(2,90)

7.33 Reactions

Sulfamate ion reacts rapidly, smoothly, and completely with nitrous acid to give N_2:(104)

$$HNO_2 + NH_2SO_3^- \longrightarrow N_2 + SO_4^= + H_2O + H^+.$$

Warm concentrated nitric acid reacts with sulfamic acid to produce N_2O gas.(90)

Dichromate, permanganate, and ferric chloride do not attack sulfamic acid.(2,83,104)

A 0.1 M sulfamic acid solution ozonated for six hours at room temperature decomposes to the extent of only a few per cent.(177)

8. Ferrous Sulfamate

8.1 Introduction

Ferrous ion is used in the Redox process for the selective reduction of plutonium to the hexone-insoluble Pu(III) state (see Section A), and is supplied by commercially available ferrous ammonium sulfate.

The alternative to ferrous ammonium sulfate is the combined reducing agent and holding reductant, ferrous sulfamate. This substance is not commercially available, and if required, must be prepared on the plant

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site by dissolving hydrogen-reduced iron powder in sulfamic acid.

8.2 Physical properties of ferrous sulfamate

Formula	$Fe(SO_3NH_2)_2$
Molecular weight	248.03
Appearance	The 2.5 M solution is greenish-blue in color.(164)
Solubility	The saturation concentration in water is in the range of 3.6 to 3.8 M at 25°C.(164)

8.3 Reactions and stability

High pH contributes to the stability of sulfamate ion towards hydrolysis, while low pH is necessary for the stability of ferrous ion towards air oxidation and consequent precipitation. The stability of ferrous sulfamate toward ferric precipitation is satisfactory upon maintaining the pH at 2 or slightly less with a 2 to 3 per cent excess of sulfamic acid.(164) The overall stability of a ferrous sulfamate solution maintained at a pH of 2 in a vessel containing an inert-gas blanket is limited by the rate of hydrolysis of sulfamate ion. This rate, as reported in 7.32, above, is approximately 0.1 per cent per day at room temperature, and increases to over 4 per cent per hour at 80°C. The total amount of sulfate ion in the solution due to hydrolysis will be the sum of that produced during the preparation of the ferrous sulfamate (approximately 1% of initial sulfamic acid) plus that produced on aging.

The reaction between sulfamate ion and nitrous acid, described under sulfamic acid (see above), is the reaction which prevents the oxidation of Fe(II) to Fe(III) through an autocatalytic mechanism involving nitrite ion.(104,118) In 5.0 M HNO_3, where oxidation of Fe(II) to Fe(III) is normally rapid, sulfamate ion maintains the half-life of Fe(II) in the range of 30 to 50 hours.(184)

In a solution initially 0.9 M $Al(NO_3)_3$, 0.3 M HNO_3, 0.05 M Fe(II), and 0.05 M sulfamate ion, 16 per cent of the total iron is converted to Fe(III) after 25 days at 20 to 25°C. A similar solution, 1.5 M in $Al(NO_3)_3$, contains 15 per cent of the total iron as Fe(III) after 5 days, thus still exhibiting satisfactory stability for convenient make-up of IBX-type solutions.(104)

The oxidation of Fe(II) proceeds more rapidly in the presence of hexone presumably due to the presence of an increased concentration of nitrous acid. The ferrous iron in a solution initially 2 M $Al(NO_3)_3$, 0.3 M HNO_3, 0.05 M Fe(II), and 0.05 M sulfamate ion, is more than 50 per cent oxidized to Fe(III) when agitated at 25°C. for 8 days with 10 volumes of hexone. The requirement of stability, however, for a 4-hour column contact is adequately met.(104)

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8.4 Preparation

Ferrous sulfamate is prepared from hydrogen-reduced iron powder and an aqueous solution of sulfamic acid by the following reaction:(24,26)

$$Fe + 2HSO_3NH_2 \longrightarrow Fe(SO_3NH_2)_2 + H_2 + 24{,}600 \text{ calories.}$$

A standardized procedure for this preparation is described in Chapter VIII.

9. Interfacial Tension and Phase Disengaging Times

9.1 Introduction

The process of liquid-liquid countercurrent extraction involves intimate contact between two essentially immiscible liquids, during which time the solute is transferred from one phase to the other across the phase boundary between the two systems. This desired contact is obtained in the Redox process by dispersing, in the continuous phase, fine droplets of the organic phase which, due to the large specific gravity differential, rise vertically through the more dense, descending aqueous phase. Interfacial tension in such a system, analogous to surface tension in distillation and absorption processes, influences the size of the droplets of the discontinuous phase. Smaller droplets are more easily formed with systems of lower interfacial tension, the droplet diameter being proportional to the interfacial tension. Small droplet diameters, in turn, mean increased interfacial area resulting in increased solute mass transfer rates across the interface. The final result is manifested in lowered H.T.U. values.

Too fine a dispersion however, which may result in the formation of an emulsion, is not desirable, owing to the corresponding increased difficulties of phase separation which outweigh any advantages resulting from the increased interfacial area.(16)

The determination of the emulsion-forming properties of a system is made by measuring the time required for the phases to disengage. The disengagement time correlates approximately with extraction column flooding capacity and entrainment losses. There seems to be no indirect method of determining disengaging times, since no reliable experimental correlation has been found between interfacial tension, density, pH, etc. of process streams and their disengaging times.

9.2 Interfacial tension

The range of interfacial tension varies from about 11 dynes per cm. for a water-hexone interface(114) to 5.5 dynes per cm. for the interface between aqueous 2.0 M $UO_2(NO_3)_2$, 0.3 M HNO_3, 0.3 M $Al(NO_3)_3$, and equilibrated hexone.(145)

Interfacial tension at the extractant, scrub, and feed points of Redox columns are given below for the ANL June, 1948 Flowsheet.(82)

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Column	Interfacial Tension, Dynes/Cm. Extractant Inlet	Scrub Inlet	Feed Inlet
IA	7.8	9.8	6.5
IB	10.3	11.0	9.8
IC	11.3	---	7.8
2A	11.9	11.0	11.9
2B	11.6	---	11.1

9.3 Disengaging time

Disengaging time has been arbitrarily defined as the time required for the separation of an organic from an aqueous phase, when the two have been combined in the appropriate ratio (usually the flowsheet ratio) to a total volume of 50 ml. and inverted in a stoppered 50-ml. graduated cylinder at the rate of once per second for 20 seconds.(207) Typical disengaging times of IAFS - IAX systems are given below as a function of flowsheet compositions (IAFS is defined as the aqueous phase composition at the IA Column feed inlet):(178)

Disengaging Times - IA Column Systems*

Flowsheet IAFS	Disengaging Time, Seconds
ANL June, 1948	15
ANL June, 1948	16
ORNL June, 1949	20
ORNL June, 1949	20
HW No. 4	16
HW No. 4	14

*)These data were obtained with solutions from column runs made with no sodium dichromate in the IAFS.

Acid-deficient systems generally exhibit disengaging times about 10 to 15 per cent higher than corresponding ANL Flowsheet systems.

Ozonolysis of dissolver solution produces no significant difference in the disengaging time when compared with an untreated solution.(187)

Although disengaging times for the IA Column as low as 14 seconds have been observed, a range from 15 to 25 seconds has proved satisfactory for column operation. Times exceeding 34 seconds indicate the presence of impurities which cause emulsification in the IA Column and generally reduce the flooding capacity of the column to as low as 50 to 75 per cent of the normal capacity.

9.4 Emulsifying impurities

The presence of emulsifying agents in minute quantities has been

noted to cause wide variation in the disengaging times of systems of essentially identical macro-composition. With IAFS-IAX disengaging time as the experimental criterion, an emulsifying impurity has been found to originate in the metal dissolving step, prior to IAF make-up.(160) This impurity, siliceous in nature, probably results from the Al-Si slug jacket bonding material, and tends to remain in the aqueous phase during extraction. However, when the dissolver solution is treated before use with a scavenger such as Super Filtrol, it is found that disengaging times return to normal.(160,182) In contrast, MnO_2 scavenging does not appear to have an appreciable effect on the disengaging time.(205)

10. Heats of Extraction

10.1 Introduction

The transfer of uranium and nitric acid from an aqueous phase into hexone is accompanied by the liberation of heat, and the reverse transfer, from hexone to aqueous, results in the absorption of heat. These phenomena are observed during the operation of the IA and IC Columns, respectively, and are of interest since distribution ratios, E_d, of uranium, plutonium, fission products, and nitric acid, show a decrease with an increase in the temperature of the system (see Section C).

The following calorimetric data apply at room temperature and are the average heats for transfer from initial compositions to equilibrium.

10.2 Uranyl nitrate

The heats of extraction of several systems containing uranyl nitrate are tabulated below:(156)

Initial Composition		Average ΔH^*,
Hexone Phase	Aqueous Phase	Gram Cal./Mole of $UO_2(NO_3)_2$
0.5 M HNO_3	1.0 M $UO_2(NO_3)_2$ 0.3 M HNO_3 2.82 M $Al(NO_3)_3$	-5800
0.5 M $UO_2(NO_3)_2$ 0.1 M HNO_3	H_2O	+2900
0.5 M $UO_2(NO_3)_2$ 0.1 M HNO_3	0.3 M HNO_3 0.82 M $Al(NO_3)_3$	+3340
0.5 M $UO_2(NO_3)_2$ 0.1 M HNO_3	1.3 M $Al(NO_3)_3$	- 460

*) $+\Delta H$ = Heat absorbed.

Values of -6000 and +3500 calories per mole of uranium transferred have been obtained from the operation of IA and IC Columns, respectively, under conditions of the ANL June 1948 Flowsheet.(159,168) However, a

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variation of IC Column inlet stream temperatures over the range from 19° to 33°C. results in no significant change in uranium H.T.U. or H.E.T.S. values.(163)

10.3 Nitric acid

The heats of extraction of several systems containing nitric acid are tabulated below:(156, 160)

Initial Composition		Average ΔH^*
Hexone Phase	Aqueous Phase	Gram-Cal./ Mole HNO_3
0.5 M HNO_3	H_2O	+ 70
0.5 M HNO_3	0.3 M HNO_3 0.82 M $Al(NO_3)_3$	nil
Hexone	1.0 M HNO_3	-1200

*) + ΔH = Heat absorbed.

The last figure, -1200 calories per mole for the heat evolved by the system on the transfer of nitric acid from water to hexone, takes into account the heats of transfer of water into hexone and hexone into water.

10.4 Hexone and water

The ΔH's of solution of water in hexone and hexone in water from the pure compound to saturation are +1800 and -2250 calories per mole of solute, respectively.(160) These values are not appreciably affected by the presence of other solutes.

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C. HEXONE-AQUEOUS PHASE EQUILIBRIA

1. Uranium

1.1 Introduction

The successful separation of uranium, plutonium, and fission products, in the Redox solvent-extraction process, is dependent upon the distribution ratios of the individual materials between the aqueous and organic phases as a function of the composition of the phases involved in the transfer system. The following tables and figures illustrate the dependency of uranium distribution upon the process variables. A discussion of the basic principles involved in the separations process, and the choice of optimum operating conditions, are presented in Section A of this chapter.

1.2 IA Column conditions

1.21 Effect of salting agent

The salting agent employed in the Redox process is aluminum nitrate. Its function is to increase the distribution of both plutonium and uranium into the organic phase. The uranium salting effectiveness of some alternate salting agents is compared with $Al(NO_3)_3$ in Figure IV-30. For a given salting effectiveness, as measured by the distribution ratio, $Al(NO_3)_3$ and $Ca(NO_3)_2$ are further removed from saturation and are thus superior to NH_4NO_3. The effect of $NaNO_3$ has been determined and compared to $Al(NO_3)_3$(171). The salting strength of 2 M $NaNO_3$ is found to be equivalent to 0.47 M $Al(NO_3)_3$ for 0.1 M $UO_2(NO_3)_2$ solutions, and equivalent to 0.40 M $Al(NO_3)_3$ for 1.5 M $UO_2(NO_3)_2$ solutions. The salting strengths of mixtures of $Al(NO_3)_3$ and $NaNO_3$ are additive functions of the salting strengths of the individual salts.

1.22 Effect of nitric acid concentration

The distribution of uranium as a function of the nitric acid concentration is illustrated in Figure IV-31 and Table IV-32, where the acid concentration in the system varies from 1.0 to -0.2 M. When the scrub and feed streams are acid-deficient the use of nitric acid in the extractant results in a more favorable distribution of uranium into the organic phase at low uranium concentrations (Figure IV-33). Since the acid is removed from the organic stream in the lower portion of the column, the use of an acid extractant has little effect on uranium distribution at the higher uranium concentrations prevailing near the feed point.

1.23 Effect of uranium concentration

The effect of uranium concentration on uranium distribution is shown in Figure IV-31. At low $Al(NO_3)_3$ concentrations (below 0.6 M), uranium distribution increases into the organic phase with an increase in uranium concentration, whereas at $Al(NO_3)_3$ concentrations 1 M and above, this effect is reversed, presumably due to the closer approach to 100 per cent saturation of the hexone with uranium.

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1.24 Effect of temperature

The distribution ratio of uranium as a function of temperature is given in Figure IV-34. Over the temperature range from 0 to 60°C., the uranium distribution ratio is seen to vary exponentially, increasing in favor of the organic phase at lower temperatures. Under IA Column conditions, the increase amounts to a factor of about 5 as the temperature is decreased from 60 to 10°C.

1.25 Effect of solvent impurities

The effects of five impurities which might be formed from solvent decomposition under off-standard operating conditions are shown in Table IV-35. The data show no significant effect of any of these impurities on the distribution ratio of uranium in the presence of 1.0 M $Al(NO_3)_3$ salting agent.

1.3 IA Column equilibrium diagrams

Equilibrium lines for the IA Column under the conditions stipulated in three different flowsheets (HW No.4, ORNL June, 1949, and ANL June, 1948) are given in Figure IV-36. A more favorable uranium distribution in the dilute region is found for the HW and ANL Flowsheet conditions, due to the use of an acid extractant. A more favorable uranium distribution at higher uranium concentrations is shown for the ORNL Flowsheet because of the higher salting agent concentration. The effect of $Al(NO_3)_3$ concentration on the equilibrium line for the HW Flowsheet is shown in Figure IV-37, while Figures IV-38 and IV-39 illustrate this effect for the ORNL and ANL Flowsheets. The $Al(NO_3)_3$ concentrations given include the equivalent salting effect of the $NaNO_3$ formed during the preparation of acid-deficient solutions by neutralization with NaOH.

1.4 IC Column conditions

1.41 Effect of nitric acid concentration

Uranium distribution as a function of nitric acid concentration under IC Column conditions is shown in Figure IV-40. Distribution into the aqueous phase increases with decreasing nitric acid concentration in the aqueous phase. With an aqueous phase containing 300 g./l. $UO_2(NO_3)_2 \cdot 3H_2O$(UNT), the uranium distribution ratio (aq./org.) increases from 4 to 20 as the aqueous phase HNO_3 concentration is decreased from 70 to 0 g./l. This effect is more pronounced at low uranium concentrations (see 1.42, below).

1.42 Effect of uranium concentration

The effect of uranium concentration on uranium distribution under IC Column conditions, is given in Figures IV-31 and IV-40. Uranium distribution into the aqueous phase is markedly increased by a decrease in uranium concentration. As the aqueous phase $UO_2(NO_3)_2$ concentration is decreased from 100 to 10 g./l., a hundred-fold increase of uranium distribution into the aqueous phase is noted.

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1.43 Effect of temperature

The absorption of heat during IC Column operation results in a lowering of the temperature of the system. The relatively small effect of temperature on uranium distribution under IC Column conditions is shown in Figure IV-34. Uranium distribution into the organic phase is seen to increase by a factor of about 2 as the temperature is decreased from 60 to 0°C.

1.5 IC Column equilibrium diagrams

Equilibrium lines for IC Column operation for varying nitric acid concentrations, are shown in Figure IV-41. The range of nitric acid concentration, 0 to 70 g./l. in the aqueous phase, is sufficient to permit estimation of uranium equilibria under conditions other than standard. The slopes of the equilibrium lines vary from 0.85 for X values above 0.6, to a value approaching 0 in the dilute region. For X values above 0.6 the slopes are independent of the aqueous phase nitric acid concentration, whereas, for X values in the range from 0 to 0.1, the equilibrium line slopes increase by a factor of about 10 (from 0.005 to 0.055) as the nitric acid concentration increases from 0 to 45 g./l.

2. Plutonium

2.1 Introduction

As with uranium, the solvent-extraction characteristics of plutonium are dependent upon the temperature and chemical compositions of the organic and aqueous phases comprising the system of which it is a part. There is, however, in the case of plutonium, the more important consideration of valence state, since the change in distribution ratio with change of Pu valence provides the principle on which is based the separation of plutonium from uranium and fission products in the Redox process.

Much of the data reported on Pu distribution resulted from tracer investigations in which oxidizing and reducing impurities present in trace amounts may have changed the Pu oxidation state. Experiments using macro amounts of Pu more nearly approach column conditions since an appreciable change in oxidation state is less probable. Apparent inconsistencies in Pu distribution data are attributed to this phenomenon.

2.2 Plutonium (VI) distribution

2.21 Effect of salting agent

Aluminum nitrate is an efficient salting agent for plutonium (VI), as shown in Figure IV-42. At a fixed uranyl nitrate concentration, the plutonium (VI) distribution coefficient (organic/aqueous) increases with increasing aluminum nitrate concentration in the aqueous phase. An aqueous solution 1.5 molar in $Al(NO_3)_3$ is approximately equal in salting strength to an 8.0 M NH_4NO_3 solution, as shown below.(63)

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Salting Agent	Concentration of Salting Agent, Moles/Liter in Aqueous Phase	Plutonium (VI) Distribution Ratio, G./L. Org. / G./L. Aq.
NH_4NO_3	3.0	0.455
"	5.0	2.08
"	8.0	10.53
$Al(NO_3)_3$	0.5	0.076
"	1.0	1.32
"	1.5	9.09

Aqueous phase: 0.0 M $UO_2(NO_3)_2$, 0.0 M HNO_3.
Organic phase: Pretreated hexone.

In general, for constant acidity and uranyl nitrate concentration, the distribution coefficient varies as a straight-line relationship on a log-log plot against salting strength expressed as aluminum nitrate or total nitrate concentration.

2.22 Effect of nitric acid concentration

Nitric acid in the aqueous phase increases the distribution ratio of plutonium (VI) in the organic phase as shown in Figure IV-42, but, other factors remaining constant, is somewhat less effective than aluminum nitrate.

2.23 Effect of plutonium concentration

The distribution ratio of plutonium (VI) is not significantly affected by changes in the total plutonium concentration in the range of compositions found in the Redox process, i.e., from 50 counts per minute per milliliter to 1.0 gram per liter.(63,69,118,156)

2.24 Effect of uranium concentration

In neutral or acid-deficient systems 0.5 to 1.0 M in aluminum nitrate the distribution ratio of plutonium (VI) exhibits a minimum value when plotted as a function of the concentration of uranyl nitrate in the aqueous phase. (See Figure IV-42.) In the presence of 1.0 to 2.0 M aluminum nitrate, the Pu distribution ratio decreases almost linearly with increasing uranyl nitrate concentration, due to the "back salting" effect on plutonium of the uranyl nitrate in the organic phase.

2.25 Effect of temperature

It has been shown that temperature changes in the range from 5 to 40°C. effect plutonium (VI) distribution. (69) The following data are measurements on ammonium nitrate systems, but the effect is paralleled in systems containing aluminum nitrate:

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Column Conditions Simulated	Temperature, °C.	Plutonium (VI) Distribution Ratio, G./L. Organic / G./L. Aqueous
IA Feed Plate(a)	7	0.417
	25	0.833
	39	0.833
2A Feed Plate(b)	5	11.23
	25	9.70
	40	7.25

(a) Aqueous phase before equilibration: 4.0 M NH_4NO_3, 0.9 M $UO_2(NO_3)_2$, 0.5 M HNO_3, 0.1 M $Cr_2O_7^=$, 100 mg./l. Pu (VI).

(b) Aqueous phase before equilibration: 8.0 M NH_4NO_3, 1.0 M HNO_3, 0.1 M $Cr_2O_7^=$, 500 mg./l. Pu (VI).

Unpublished work by the Chemical Research Section indicates that the distribution ratio of plutonium (VI) (organic/aqueous), under conditions approximating the 2A Column varies inversely with temperature, decreasing by a factor of from 4 to 10 as the temperature is raised from 0.to 60°C. However, at high uranium concentrations e.g., under IA conditions, this tendency is reversed, and at 1.0 M $UO_2(NO_3)_2$ and 1.3M $Al(NO_3)_3$ in the aqueous phase, the distribution ratio of plutonium (VI) increases slightly as the temperature increases, changing from 0.95 at 0°C. to 1.1 at 60°C.

2.26 Effect of solvent impurities

Neither methyl isopropyl diketone nor mesityl oxide exerts a significant effect on the distribution of plutonium (VI).(147,151) The effects of acetic acid and other hexone decomposition products are shown in Table IV-35.(174) Acetic acid (0.6 M) in hexone increases the distribution ratio of Pu (VI) to about 1.1 as compared with 0.6 in the absence of the acid. Ethyl nitrolic acid (5 g./l. in hexone) increases the distribution ratio from 0.62 to 0.97, while the other impurities listed do not appear to have any appreciable effect.

2.27 Effect of minor components

Apart from reduction and holding oxidant effects, neither sulfamic acid nor sodium dichromate has an appreciable effect on the distribution of plutonium (VI).(104,192)

2.3 Plutonium (V) distribution

The chemistry of plutonium (V) has been found to be similar to that of neptunium (V) and uranium (V).(10) Therefore, due to the inextractability of neptunium (V), and to the fact that Pu (V) forms no nitrate

complexes,(139) it is believed that plutonium (V) is relatively inextractable into hexone.(86,117) The distribution ratio (organic/aqueous) is estimated to be about 10-3.(85)

2.4 Plutonium (IV) distribution

2.41 Comparison with other oxidation states

Plutonium (IV) is extracted into hexone under the same conditions as Pu (VI), but the distribution ratios are somewhat smaller, as shown below.(81,167,192)

Aqueous Composition, M(a)			Distribution Ratio, G./L. Organic / G./L. Aqueous	
$Al(NO_3)_3$	$UO_2(NO_3)_2$	HNO_3	Pu (IV)	Pu (VI)
1.3	1.0	0.0	0.36	1.09
1.0	0.0	0.3	2.01	3.65
2.0	0.5	-0.2	0.19	2.16
1.0	1.0	-0.2	0.04	0.89

(a) Aqueous composition after equilibration with pretreated hexone.

In the Redox process, the distribution ratio of plutonium (IV) is expressed in the following general equation:

$$\log_{10} E_a^o = 1.0185 + 2.5685 \log_{10} C_{NO_3^-} - 0.6307\ pH - 1.25\ C_{UO_2(NO_3)_2},$$

where the concentrations (C) are expressed in moles per liter in the aqueous phase.(192)

A more specific relationship from which the distribution ratios may be calculated in systems which contain no uranium and in which the distribution ratio (organic/aqueous) of plutonium (IV) is greater than unity, is given by:

$$\log_{10} E_a^o = -1.2057 + 3.0425 \log_{10} C_{NO_3^-} - 0.3661\ pH,$$

where $C_{NO_3^-}$ represents the total nitrate concentration in the aqueous phase in moles per liter.(192)

2.42 Effect of salting agent

Aluminum nitrate is an effective salting agent for plutonium (IV), as shown by Figure IV-43, where the Pu distribution ratio is given as a function of the concentration of aluminum nitrate in the aqueous phase.(53) An increase in aluminum nitrate concentration from 0.2 M to 1.3 M in the aqueous phase, increases the distribution of plutonium (IV) into the organic phase by a factor of about 300. This figure also illustrates the comparative effects of some alternate salting agents.

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2.43 Effect of nitric acid concentration

Nitric acid has much the same effect on the hexone extraction of plutonium (IV) as it has on that of plutonium (VI), as shown in Figure IV-44, where an increase in nitric acid concentration in the aqueous phase is accompanied by a corresponding increase in the distribution ratio of Pu (IV) in the organic phase.(54,84,118 192)

2.44 Effect of plutonium concentration

The data concerning the effect of plutonium concentration on the distribution ratio of Pu (IV) are erratic and inconclusive. It has been stated that in the absence of oxidizing and reducing agents Pu (IV) distribution ratios are not significantly affected by changes in total Pu concentration from 1.5×10^{-4} to 1.46 grams per liter in the organic phase.(192)

2.45 Effect of uranium concentration

The distribution ratio of plutonium (IV) as a function of uranyl nitrate concentration in the aqueous phase is shown in Figure IV-44.(192) In neutral or acid-deficient regions, the value of the distribution ratio passes through a minimum at approximately 0.02 M uranyl nitrate concentration. At 0.3 M to 0.6 M nitric acid, the distribution ratio decreases uniformly with increasing uranyl nitrate concentration.

2.46 Effect of temperature

The change in plutonium (IV) distribution with temperature roughly parallels that of plutonium (VI). From 0.3 M nitric acid solutions 1.3 M in aluminum nitrate, the Pu (IV) distribution coefficient decreases by a factor of 2 to 5 with a change in temperature from 0 to 60°C. In acid-deficient solutions, this distribution coefficient becomes very small, and the temperature coefficient becomes correspondingly less important.(142)

2.47 Effect of solvent impurities

The effect of hexone impurities on the distribution of plutonium (IV) is shown in Table IV-35.(174)

2.48 Effect of minor components

The concentration of sulfamic acid in the aqueous phase does not exert a significant effect on plutonium (IV) distribution.(104,192)

2.5 Plutonium (III) distribution

The distribution ratio of plutonium (III), E_a^o, is 4.5×10^{-4} between hexone and a 1.3 M $Al(NO_3)_3$ solution which is 0.2 M acid-deficient.(81,139,192) It is not affected by nitric acid, uranyl nitrate, or plutonium concentration in the aqueous phase.(81)

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2.6 Equilibrium lines

Equilibrium lines for Pu(IV) and Pu(VI) in the IA Column for HW No. 4 Flowsheet, ANL June, 1948 Flowsheet, and ORNL June, 1949 Flowsheet conditions, and in the 2A and 2B Columns for HW No. 4 Flowsheet conditions are shown in Figures IV-45, IV-46, IV-47, IV-48, and IV-49. These equilibrium lines were determined by stagewise calculation methods. For the IA Column, the calculations were based on the assumption that one plutonium stage is equivalent to one uranium stage, and that plutonium distribution depends only on the concentrations of uranyl nitrate, nitric acid, aluminum nitrate, and sodium nitrate, in the aqueous phase. The concentrations of these components at each stage were estimated from the results of batch-countercurrent equilibrium studies made with "cold" uranium for each of the three flowsheets.(150,173,175) Pu(IV) and Pu(VI) distribution ratios for each stage were estimated by interpolating between points on plots of Pu(IV) and (VI) distribution data (167,192,198) similar to Figures IV-42 and IV-44. For the 2A and 2B Columns, the calculations were based on the assumptions that one plutonium stage is equivalent to one nitric acid stage, and that plutonium distribution depends only on the concentrations of aluminum nitrate and nitric acid in the aqueous phase. Nitric acid concentrations at each stage were estimated from 2A and 2B Column nitric acid operating diagrams similar to those appearing in Chapter V. Aluminum nitrate concentrations in the 2A Column were assumed to be 1.3 M in the extraction section and 1.26 M in the scrub section. Pu(IV) and Pu(VI) distribution ratios were estimated from data reported by the Hanford Works Chemical Research Section.(167,192) By means of these distribution ratios and equations for the Pu(IV) and Pu(VI) operating lines for flowsheet conditions, X and Y equilibrium curves were then constructed by drawing smoothed curves through these points.

The IA Column will normally operate on feed containing Pu(VI) only, and the Pu(IV) equilibrium lines (dashed lines) on Figures IV-45, IV-46, and IV-47 are shown only to illustrate that this column cannot extract Pu(IV) without large waste losses. The loop in the extraction section Pu(IV) equilibrium lines for the HW No. 4 and ANL Flowsheets (Figures IV-45 and IV-46) is caused by the difference in nitric acid concentrations between the bottom and top portions of the extraction section. Pu(IV) equilibrium favors the aqueous phase in the upper portion of the extraction section, because this portion is low in acid, while Pu(IV) equilibrium favors the hexone phase in the lower portion which contains a higher nitric acid concentration. The net result is that any Pu(IV) present in the IA Column will reflux under the conditions of these flowsheets, reaching concentrations in the center stages of the extraction section approximately 5 to 20-fold higher than the IAF Pu(IV) concentration, and more than 50 per cent of the Pu(IV) will be lost to the IAW. Pu(IV) does not reflux under the conditions of the ORNL Flowsheet (Figure IV-47) since the entire column is acid deficient and Pu(IV) equilibrium favors the aqueous phase. Thus, virtually all Pu(IV) would be lost to the IAW under the conditions of this flowsheet.

The 2A and 2B Columns can operate satisfactorily on either Pu(IV) or Pu(VI). Both columns were designed to extract the valence state with the most unfavorable equilibrium relationships (Pu(IV) in 2A, Pu(VI) in

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2B). The equilibrium lines for the design valence state are shown as solid lines on Figures IV-48 and IV-49, while the equilibrium lines for the other valence states are shown as dashed lines.

3. Neptunium

3.1 Effect of salting agent

Under acid flowsheet conditions, aluminum nitrate is an effective salting agent for both Np (IV) and Np (VI).(36) However, under acid-deficient conditions the stable species is Np (V) which is relatively hexone inextractable, as shown below:(36,39)

System Simulated	Initial Composition of Aqueous Phase, M				Np Distribution Ratio, G./L.Organic / G./L.Aqueous
	$Al(NO_3)_3$	HNO_3	$Cr_2O_7^=$	$UO_2(NO_3)_2$	
IA Scrub (acid)	1.3	0.21	0.01	0.5	4.00
IA Extraction (acid)	0.7	0.15	0.05	0.5	1.30
IA Scrub (acid-deficient)	2.0	-0.2	0.05	0.5	0.12
IA Extraction (acid-deficient)	1.0	-0.2	0.00	0.5	0.012
IB Extraction (acid) (0.05 M $Fe(NH_2SO_3)_2$)	1.3	0.14	0.00	0.5	0.05

Organic phase: Neutral hexone, except IA extraction system is 0.5 M HNO_3.

3.2 Effect of nitric acid concentration

Neptunium is salted into the organic phase by small concentrations of nitric acid. In neutral or acid-deficient systems neptunium favors the aqueous phase under both oxidizing and reducing conditions.(36)

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Conditions	Composition of Aqueous Phase, M $Al(NO_3)_3$	$UO_2(NO_3)_2$	HNO_3	Np Distribution Ratio, G./L. Organic / G./L. Aqueous
0.05 $Na_2Cr_2O_7$	0.7	0.0	0.0	0.3
"	0.7	0.0	0.5	1.7
"	0.7	1.0	0.0	0.7
"	0.7	1.0	0.5	1.5
0.05 $Fe(NH_2SO_3)_2$	1.3	0.0	0.0	3×10^{-3}
"	1.3	0.0	0.5	1.5
"	1.3	0.3	0.0	2×10^{-3}
	1.3	0.3	0.5	0.35

3.3 Effect of uranium concentration

With increasing uranium concentration, under acid flowsheet conditions, the distribution of Np into the organic phase decreases slightly both in the extraction and scrub sections of the IA Column. Under acid-deficient conditions, however, increasing uranium reduces the Np distribution ratio, E_a^o, (as shown in the following table) in the scrub section of the IA Column but increases it in the extraction section. Typical IA-system Np distribution ratios are tabulated below.(36)

Composition of Aqueous Phase, M $UO_2(NO_3)_2$	$Al(NO_3)_3$	HNO_3	$Cr_2O_7^=$	Np Distribution Ratio, G./L. Organic / G./L. Aqueous
Scrub Conditions:				
0.0	2.0	-0.20	0.05	8
0.5	2.0	-0.25	0.05	0.1
0.0	1.3	0.21	0.01	16
0.5	1.3	0.21	0.01	4
Extraction Conditions:				
0.0	1.0	-0.10	0.05	0.001
0.5	1.0	-0.15	0.05	0.01
1.0	1.0	-0.20	0.05	0.02
0.0	0.7	0.15	0.05	1.8
0.5	0.7	0.15	0.05	1.3
1.0	0.7	0.15	0.05	1.3

Organic phase: Neutral hexone, except in acid extraction systems (last 3 lines of table), where it was 0.5 M HNO_3.

In an acid IB Column the distribution ratio of Np is constant at about $0.05(E_a^o)$.

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4. Fission Products

4.1 Introduction

One of the important bases of the Redox solvent-extraction process for the separation and purification of uranium and plutonium from fission products is the fact that, with the exception of ruthenium under certain conditions, fission products are not readily extracted into the hexone phase as are uranium and plutonium. The following data show the effects of operating variables on fission-product distribution and are to be compared to Subsections C1 and 2 for uranium and plutonium distribution.

Emphasis in this subsection is placed on the fission products Ru, Ce, and the related pair, Zr + Nb. The decontamination factors for these fission products have proved to be the least satisfactory in the Redox solvent-extraction process. Zr and Nb are considered as one, partly due to their common decay chain (see Appendix A) and partly due to the fact that Hanford-level runs at ORNL(138) have shown that the decontamination factors for both elements are essentially the same throughout two solvent-extraction cycles.

All distribution ratios in this subsection are given as $\frac{\text{G./L. Organic Phase}}{\text{G./L. Aqueous Phase}}$, and henceforth, will be designated by the symbol, E_d.

The distribution ratios for the various fission products are presented first and translation of these distribution data into decontamination factors are taken up at the end of this subsection.

4.2 Gross beta

The distribution of gross beta radioactivity between hexone and water in the Redox process is distinct from the distribution of gross gamma radioactivity. This is due to the fact that the individual fission products have characteristic radiations which differ from the radiations of other fission-product elements in three principal ways: (a) type of radiation (whether beta, gamma, or both); (b) energy of the radiation (which affects counting efficiency, as discussed in Chapter II); and (c) half life of the radioactive fission product in question. The net effect of the first two variables is to alter the ratio of specific countable beta radioactivity to that of specific gamma radioactivity between the various fission products. This ratio of beta to gamma radioactivity in a mixture of fission products will change also as a function of time elapsed after discharge from the piles, due to the third variable. Other factors which affect the beta-to-gamma ratio in a mixture of fission products are the pile power level, duration of irradiation, and the neutron capture cross-section of the individual fission-product isotopes. The latter variables are beyond the scope of this chapter.

Typical beta-emitting fission-product distribution ratios are given below for an extraction and five scrub stages.(137)

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	Extraction Stage	Scrub Stages 1	2	3	4	5
Distribution Ratio, E_a^o:						
Gross Beta	0.001	0.035	0.047	0.057	0.076	0.10
Ru	0.017	0.034	0.034	0.048	0.074	0.09
Overall D. F.	215	607	1.3×10^3	3.1×10^3	5.5×10^3	10.9×10^3

Feed: (4 vol.) 1.3 M $Al(NO_3)_3$, 0.05 M acid-deficient, 0.03 M $UO_2(NO_3)_2$.

Scrub: (1 vol.) 1.3 M $Al(NO_3)_3$, 0.05 M acid-deficient.

Solvent: (10 vol.) Hexone.

The change in gross beta distribution with the number of scrub stages closely parallels that of Ru distribution. The low concentration of uranyl nitrate (0.03 M), in the feed shown in the table above, has no significant effect on gross beta distribution due to the small effect of uranyl nitrate upon Ru distribution.

Beta-emitting fission-product decontamination factors after head-end treatment (Ru volatilization and MnO_2 scavenging) plus first Pu and first U cycles are included in Reference (121).

4.3 Gross gamma

4.31 Effect of salting strength and acidity

The effect of $Al(NO_3)_3$ and HNO_3 concentration on total gamma-emitting fission-product distribution, is shown in Figure IV-50.(129) At an initial nitric acid concentration of 0.2 M in the aqueous phase, the gamma-emitting fission-product distribution ratio, E_a^o, increases from 5×10^{-4} to 3.5×10^{-1} as the aqueous $Al(NO_3)_3$ concentration increases from 0.0 to 2.5 moles per liter. With 1.25 M $Al(NO_3)_3$ in the aqueous phase the gamma-emitting fission-product distribution ratio decreases from 2.5×10^{-1} to 6.0×10^{-4} as the initial concentration of HNO_3 in the aqueous phase is decreased from 0.25 M acid to 0.1 M acid-deficient. Under the conditions of the solvent-extraction runs, as given in Figure IV-50, the distribution ratio, E_a^o, levels off at high $Al(NO_3)_3$ concentrations and at negative free-acid concentrations.

Nitric acid functions much more efficiently as a salting agent for fission products than it does for uranium; therefore, low acid concentrations tend to result in improved decontamination.(129) This effect is shown in Figure IV-51 where the separation factor (U distribution ratio/fission-product distribution ratio) is plotted against $Al(NO_3)_3$ concentration at various HNO_3 concentrations.(137) The effect of $Al(NO_3)_3$ concentration on the decontamination factor, however, varies in a manner different from that of the separation factor. Under acid-deficient flowsheet conditions (-0.2 M HNO_3 in the IAFS)

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the gamma D.F. increases with an increase in the $Al(NO_3)_3$ concentration up to about 1.4 M $Al(NO_3)_3$ and then begins to decrease. Under acid flowsheet conditions (0.2 M HNO_3 in the IAFS) the gamma D.F. increases with increasing $Al(NO_3)_3$ concentration only to about 1.0 M $Al(NO_3)_3$ before beginning to decrease. The relationship between the decontamination factor and the separation factor is given by the equation shown in Figure IV-59.

Figure IV-52 is a nomograph relating the gamma-emitting fission-product distribution ratio to $Al(NO_3)_3$ and HNO_3 concentration.(135)

4.32 Effect of temperature

An increase in temperature decreases the gamma-emitting fission-product distribution ratio, E_a^o, exponentially at approximately the same rate as it does for uranium.(129) The gamma-emitting fission-product distribution ratio decreases from 0.014 at 14°C. to 0.005 at 57°C. when the initial aqueous composition is 1.25 M $Al(NO_3)_3$, 0.45 M HNO_3, 0.02 M $UO_2(NO_3)_2$, and 0.1 M $Na_2Cr_2O_7$; the solvent is neutral hexone; and the radioactive source, irradiated U^{235} aged 6 weeks.

The overall effect of decreasing the uranium and fission-product distribution ratios, E_a^o, by the same percentage is to increase the decontamination factor. This may be calculated for a single batch contact by the equation given in Figure IV-59.

4.4 Ruthenium

4.41 Chemical species of ruthenium in process solutions

Ruthenium is known to be present in Redox process solutions in several chemical species. These species have, however, been only partially characterized. In experiments at Hanford Works species of ruthenium have been differentiated according to their behavior in oxidation to RuO_4 and volatilization. In experiments at Oak Ridge National Laboratory species of ruthenium have been differentiated on the basis of their behavior in solvent-extraction. No firm correlation has been established between the systems of species distinguished by these two empirical methods.

Experiments at Hanford Works have shown at least three different ruthenium species to exist in dissolver solution. The predominant oxidation state is postulated to be Ru(IV). The weighted average distribution ratio, E_a^o, for Ru in untreated dissolver solution under IA Column feed point condition (ORNL Flowsheet) is about 0.008.(187) The three ruthenium species are designated A_1, A_2, and B. The distribution ratios for the various species together with their behavior with respect to Ru volatilization are given in Table IV-53A.

Four forms of Ru are postulated by ORNL on the basis of solvent-extraction experiments with Ru tracer: RuA, RuB, RuC, and RuD. Distribution ratios for these species under highly acid conditions together with equilibrium constants and reaction half-times between the various forms are presented in Table IV-53B.

RuD displays a distribution ratio which is most readily explained by designating it as ruthenium tetroxide, RuO_4. The compound is known

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to be sufficiently stable to display a characteristic distribution.(27) RuC is probably uncomplexed ruthenium in the +4 valence state exhibiting a distribution ratio, E_a^o, of 10^{-3} to 10^{-5} depending upon conditions. (34, 113) However, RuD or RuC are not likely to encountered in the extraction columns of the Redox Plant because residual amounts of RuO_4 remaining in the dissolver solution after the Ru volatilization step are likely to be reduced by small quantities of reducing materials such as oxides of nitrogen or Cr^{+3} (if not by Pu^{+4}), and Ru(IV), due to its strong complex-forming characteristics, is complexed by reagents such as nitrite ion.(98)

RuA and RuB are thought by ORNL to be nitroso complexes of ruthenium, and correlation of available data indicates that RuB corresponds to the Hanford Works' ruthenium species B (see Table IV-53). Ruthenium species B is present in 10-day old dissolver solution to the extent of ca. 5 per cent of the total ruthenium as shown in Table IV-53A. It is a difficultly volatilized form of Ru and constitutes most of the ruthenium remaining in dissolver solution after a 6-hour volatilization at 95°C.(187) Under acid-deficient flowsheet conditions the ruthenium species B distribution ratio, E_a^o, for extraction is about 0.002. This value is in approximate agreement with the distribution ratio, E_a^o, of about 0.001 given by KAPL (113)for the nitroso complex $RuNO(NO_3)_3$ under acid-deficient flowsheet conditions (see Sub-subsection 4.48). Ruthenium distribution as a function of nitric acid concentration is given in Figure IV-54.

ORNL's RuA, exhibiting a distribution ratio, E_a^o, under acid flowsheet conditions of about 7, is the ruthenium species responsible for the poor scrub distribution coefficients characteristically displayed by ruthenium. As indicated in Table IV-53, RuA is the dominant species present in the hexone phase after several hours' contact. The data indicate that the scrub distribution ratios, E_a^o, will increase with time until the equilibrium concentration of RuA is approached. This effect is verified in the results of HW-18415(187) in which data for the first and second scrub stages indicate an increase in the distribution ratio to a value greater than 1 in some cases, under acid-deficient flowsheet conditions. This general increase in Ru distribution ratio in successive scrub stages indicates that the elimination of ruthenium at some point in the IA Column feed preparation process is highly disirable.

4.42 Effect of salting strength

Under certain conditions, increasing the aluminum nitrate concentration from 0 to 2 M increases the distribution ratio of Ru into hexone by 40-fold in the extraction section and 4-fold in the scrub section, as shown in Figure IV-54.(137)

4.43 Effect of nitric acid concentration

The distribution ratio, E_a^o, of Ru in the extraction section decreases as much as 400-fold as the HNO_3 concentration in an $Al(NO_3)_3$-salted system is decreased from +0.2 M to -0.2 M. As shown also in Figure IV-54, the distribution ratio, E_a^o, of Ru in the scrub section decreases by a factor of 10 for a similar decrease in the HNO_3 concentration of the aqueous phase from +0.2 M to -0.2 M.

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4.44 Effect of uranium concentration

The distribution ratio of ruthenium is decreased slightly (not exceeding a factor of 3) in the IA scrub section by the presence of process concentrations of uranyl nitrate (0.476 M) in the IAP stream.(133)

4.45 Effect of minor components

Oxidation with 0.1 M $Na_2Cr_2O_7$ at 95°C. for 2 hours increases the distribution ratio, E_a^o, of Ru tracer about 2-fold between a hexone phase and an aqueous solution containing 1 M $Al(NO_3)_3$ and 0.5 M HNO_3.(131) The effect is not due to a specific impurity in the solvent, since $Na_2Cr_2O_7$ increases the distribution of Ru into dibutyl dellosolve and other solvents as well.(95)

The presence of ferrous sulfamate reduces the Ru distribution ratio, E_a^o, by a factor of from 2 to 10 between 25 and 70°C.(95) These effects may be due to the oxidation-reduction behavior of the components mentioned toward either Ru itself or toward a component such as nitrite ion.

Mesityl oxide in concentrations of from 1.0 to 3.0 weight per cent in the hexone phase slightly decreases the distribution ratio, E_a^o, of Ru in simulated IA Column extraction and scrub sections under acid flowsheet conditions.(156)

4.46 Effect of contact time

In the presence of 0.01 to 0.3 M nitric acid, the distribution ratio, E_a^o, of Ru slowly increases with increasing time of contact of the aqueous and hexone phases.(109) In a 0.2 M acid-deficient system, the distribution ratio, E_a^o, for extraction remains small ($<10^{-4}$) with time of contact up to 7 days, in either the presence or absence of dichromate.(109) The distribution ratio of Ru in the scrub sections, however, slowly increases as the number of scrub sections is increased as previously indicated, thus exhibiting a slight effect due to contact time.

4.47 Effect of temperature

At 60°C. the distribution ratio, E_a^o, for Ru is lower than the value at 25°C. by a factor of about 2 — the same reduction as that for the uranium distribution ratio.(133) This effect results in an over-all increase in the ruthenium decontamination of uranium.

4.48 Distribution of the nitrosc complex, $RuNO(NO_3)n$

The distribution ratio for ruthenium from an aqueous solution containing originally 0.001 M inactive $RuNO(NO_3)_n$, 1 M $Al(NO_3)_3$, and 0.1 M $Cr_2O_7^=$, is given in the table below as a function of the initial HNO_3 concentration in the aqueous phase.(113) The subscript n has a probable value of 3.

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Initial HNO_3 Concentration in Aqueous Phase, M	$RuNO(NO_3)_n$ Distribution Ratio, G./L. Organic / G./L. Aqueous	Final HNO_2 Concentration in Hexone Phase, M
0.31	0.384	$<10^{-4}$
0.1	0.253	$<10^{-4}$
0.01	0.087	$<10^{-4}$
-0.2	0.0007	$<10^{-4}$

The hexone phase in these determinations was pre-equilibrated with respect to HNO_3. The final HNO_2 concentration in the hexone phase was maintained at a low value in order to eliminate any source of error due to this variable.

4.5 Zirconium and niobium

4.51 Chemistry

Most of the beta radioactivity associated with uranium at the end of the first solvent-extraction cycle is due to ruthenium, while Zr and Nb are responsible for a significant portion of the gamma radioactivity.(137)

The forms of Zr and Nb in process solutions are not well understood due to their extremely low concentrations (ca. 10^{-5} M in IAF) and ease of colloid formation, and because of their complexes with fluoride, sulfate, and other ions.(137) The +4 oxidation state of Zr is the only one encountered in the Redox process. The Zr +4 ion is stable only in highly acid solutions, hydrolyzing to $Zr(OH)_2^{++}$ at a pH above 0.1.(171)

4.52 Effect of head-end treatment

After the Ru volatilization step of the feed preparation, Zr and Nb may be effectively removed (90 per cent or more) by a scavenging process, involving the precipitation of MnO_2 in the dissolver solution (from $KMnO_4$ introduced in the volatilization step) and its subsequent removal by centrifugation.(189) Countercurrent batch scavenging (3 contacts) of HW dissolver solution by Super Filtrol also results in the removal of 90 per cent or more of both Zr and Nb.(195) The following data show the effect of head-end scavenging on Zr distribution and decontamination:

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Head-End Treatment	Zr Distribution Ratio, G./L. Organic / G./L. Aqueous: Extraction	1st. Scrub	2nd. Scrub	Over-all Zr D.F.	Ref.
None	0.00018	0.012	0.15	1.6×10^5	HW-15754
None	0.00018	0.033	0.05	1.1×10^5	HW-16076
Three Contacts, Filtrol 20 g./l.; D. F. = 584	0.0022	0.007	0.19	2.7×10^7	HW-16076

(ORNL June, 1949 Flowsheet)

As the table above shows, Zr apparently becomes more hexone-extractable as the number of scrub stages is increased. This phenomenon, noted also with ruthenium, makes the head-end removal of Zr very desirable.

4.53 Effect of salting strength

The Zr-Nb distribution ratio, E_a^o, increases from 4×10^{-4} to 0.16 as the concentration of $Al(NO_3)_3$ increases from 0.25 to 2.0 M, as illustrated in Figure IV-55.(137)

4.54 Effect of nitric acid concentration

A decrease in the aqueous nitric acid concentration from 0.9 M acid to 0.1 M acid-deficient decreases the Zr-Nb distribution ratio, E_a^o, from 2 to 1×10^{-4} as illustrated in Figure IV-55.(137) It is believed that at low acidity the hydrolyzed zirconium salts are in the form of non-extractable colloids. As the acidity increases, the proportion of colloidal or otherwise aggregated zirconium in solution decreases, and in strongly acidic solutions, the Zr, as ZrO^{+2} or Zr^{+4}, is extractable into the organic phase.(85)

4.55 Effect of minor components

In the absence of dichromate, methyl isobutyl carbinol (MIBC) does not appear to have a marked effect on the distribution of Zr into hexone.(90,148) In the presence of dichromate, the Zr distribution ratio, E_a^o, increases directly with MIBC concentration under acid flowsheet conditions. The data below illustrate this phenomenon:(90)

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Per Cent MIBC in Hexone	$Zr\ E_a^o$
0.01 (or less)	0.0083
0.10	0.0118
0.10	0.0114
0.20	0.0270
0.20	0.0278
0.25	0.0345
0.25	0.0417
1.00	0.0526

Aqueous phase: 0.7 M HNO_3, 0.1 M $Cr_2O_7^=$, Zr tracer.
Organic phase: Shell hexone, specially purified.

Under acid-deficient flowsheet conditions, Zr decontamination is not sensitive to MIBC concentration.(99) Methyl isopropyl diketone and mesityl oxide have no significant effect on Zr distribution.(89)

4.6 Cerium

4.61 Effect of oxidation state

The distribution ratio, E_a^o, for Ce^{+4} from a solution 1.2 M $Al(NO_3)_3$ and 0.1 M HNO_3 is about 1, whereas the distribution ratio of Ce^{+3} is on the order of 0.5 to 0.001 depending upon conditions.(111) The vigorous oxidizing conditions of Ru volatilization, however, result in no increase in the Ce distribution ratio.(179)

4.62 Effect of salting strength

As with other fission products, the Ce distribution ratio, E_a^o, increases with increasing $Al(NO_3)_3$ concentration. Under acid flowsheet conditions the Ce distribution ratio increases exponentially from 0.07 to 0.4 as the $Al(NO_3)_3$ concentration increases from 0.8 to 1.25 M, as shown in Figure IV-56.

4.63 Effect of nitric acid concentration

The distribution of Ce as a function of HNO_3 concentration is also illustrated in Figure IV-56. With 1.24 M $Al(NO_3)_3$ in the aqueous phase, the distribution ratio, E_a^o, decreases slowly from 0.5 to 0.2 as the initial concentration of HNO_3 in the aqueous phase decreases from 1.0 to 0.2 M. The distribution ratio then decreases very rapidly in the region of stoichiometrical neutrality to become 0.001 at 0.1 M acid-deficient.(111)

4.64 Effect of uranium concentration

The distribution ratio, E8, of Ce from a mixture of $Al(NO_3)_3$ and $UO_2(NO_3)_2$ salting agents is much lower than that obtained with $Al(NO_3)_3$ alone at comparable ionic strengths. This result indicates "back-salting" of Ce into the aqueous phase by the uranium extracted into the hexone.(111)

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4.65 Effect of dichromate

The addition of $Na_2Cr_2O_7$ to a solution containing Ce^{+3} tracer, 1.2 M $Al(NO_3)_3$, and 0.15 M HNO_3, causes the Ce distribution ratio, E_g^o, to rise rapidly and pass through a maximum at about 0.002 M $Na_2Cr_2O_7$.(111) The data are plotted in Figure IV-57. Dichromate is more effective in promoting the extraction of Ce than either $KMnO_4$ or $NaBiO_3$ despite the more negative oxidation potentials of these latter oxidants, hence the conviction that the mechanism of the extraction of cerium involves $Cr_2O_7^=$ in a role other than, or in addition to, simple oxidation.(111)

4.66 Effect of cerium concentration

The addition of non-radioactive cerium nitrate, $Ce(NO_3)_3$, reduces the extraction of radioactive cerium tracer. Figure IV-58 illustrates the effect for an extraction and scrub step. The data indicate that almost complete exchange takes place between the Ce isotopes. The effect is of process importance since IAF solutions, 2.0 M in $UO_2(NO_3)_2$, contain 10^{-4} M or more of inactive Ce^{140}.(111) The concentration effect continues into the tracer region. Thus by increasing the specific radioactivity of a cerium solution from 10^2 to 10^4 cerium counts/min./ml., the distribution ratio, E_g^o, decreases by a factor of 2.

4.67 Effect of methyl isobutyl carbinol

The distribution of Ce is not appreciably affected by MIBC.(111)

4.7 Other fission products

4.71 Cesium

Distribution ratios, E_g^o, for Cs under IA Column extraction section conditions corresponding to the ANL (acid) Flowsheet are given below:(158)

Concentration of $UO_2(NO_3)_2$ in IAFS, M	Concentration of HNO_3 in IAFS, M	Cs Distribution Ratio, G./L. Organic / G./L. Aqueous
0	0.15	0.00132
0.5	0.15	0.00447
1.0	0.15	0.00891
1.0	0.45	0.00852

Aqueous phase: 0.65 M $Al(NO_3)_3$, 0.05 M $Na_2Cr_2O_7$, $UO_2(NO_3)_2$ and HNO_3 as indicated.

Organic phase: Pretreated hexone, 0.5 M HNO_3.

Experiments show that the presence of 0.3 per cent methyl isobutyl carbinol in the hexone has no effect on the distribution ratio of cesium.(148)

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4.72 Lanthanum

The distribution ratio, E_a^o, of La is on the order of 10^{-3} to 10^{-4} from a solution 5 M in NH_4NO_3 and 3 M HNO_3.(55) The effect of $Al(NO_3)_3$ salting agent is not expected to be significantly different from that of NH_4NO_3.

4.8 Fission-product distribution ratios vs. decontamination performance

4.81 Introduction

Presented below is a brief summary of representative distribution ratios for the individual fission products under Redox process conditions. The relationship which exists between individual fission-product distribution ratios and decontamination factors for a single batch contact is indicated. (See Chapter V for performance in countercurrent devices.) The relationship between individual fission-product decontamination factors and over-all required D. F.'s are treated in the form of equations and graphs, and, finally, decontamination is discussed as a function of head-end treatment.

4.82 Distribution ratios

Representative distribution ratios of several fission products and fission-product species for the extraction stage at the 1A Column feed plate are as follows: (ORNL June, 1949 Flowsheet)

Fission Product Species	Distribution Ratio, E_a^o
Total Ru(a)	0.008
Ru Species B(b)	0.0018
Zr - Nb	0.00018
Ce	0.001

(a) The fractions of each form of Ru in dissolver solution and the change of forms with aging are presented in Table IV-53.

(b) Ru species B (Hanford nomenclature) comprises the bulk of the ruthenium remaining after the RuO_4 volatilization procedure.

Ruthenium and zirconium show increased extractability into the hexone phase upon successive scrubbings. Under conditions of the ORNL June, 1949 Flowsheet the distribution ratios, E_a^o, for "unstrippable" Ru and Zr in the second scrub stage of the 1A Column are on the order of 0.5 and 0.15, respectively. Ruthenium and zirconium, therefore, will follow the organic stream, leaching out along the way, and are the fission products which limit the attainable D. F.'s in the Redox process.

4.83 Single batch D. F.

The fission-product decontamination factor effected in a U or Pu stream is dependent upon (a) fission-product distribution ratio, (b)

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U or Pu distribution ratio, and (c) the relative organic-aqueous flow rates. Assuming immiscible phases and no volume changes, the decontamination factor achieved by a single batch contact is plotted as a function of fission-product distribution ratio in Figure IV-59. Included are several U or Pu distribution ratio parameters at constant flow ratio, and one parameter showing the effect of altering the flow ratio at constant U or Pu distribution ratio. At a constant U or Pu distribution ratio, E_a^o, of 1.0 and an organic-aqueous volume ratio of 2, Figure IV-59 shows that decreasing the fission-product distribution ratio from 0.01 to 0.001 increases the single batch decontamination factor from 34 to 340. Likewise, increasing the U or Pu distribution ratio, E_a^o, or decreasing the organic-to-aqueous volume ratio is shown to increase decontamination. A more extended coverage of these factors as regards decontamination performance in countercurrent solvent-extraction devices is given in Chapter V.

4.84 Individual and over-all D. F.'s

The over-all D. F.'s for U and Pu required of the Redox process are dependent upon the irradiation history of the uranium. Assuming 360 g. Pu/ton U and a 90 day "cooling" period, the gross gamma D. F. required for Pu is 5×10^6 and the gross beta D. F. required is 1×10^7. The gross gamma and gross beta D. F.'s required for uranium are tentatively set at 2.3×10^6 and 1.5×10^6, respectively.(193)

Correlation of individual fission-product decontamination factors with the over-all decontamination of a final uranium or plutonium stream may be obtained from the following equation.(115) The decontamination factor is defined as the ratio of the initial concentration of fission products per unit weight of product to the final concentration on the same basis:

$$\text{D. F.} = \frac{\sum_1^n C_{ni}}{\sum_1^n C_{np}} = \frac{1}{\sum_1^n \frac{X_n}{(\text{d.f.})n}} \qquad \text{.....(1)}$$

where D. F. = over-all decontamination factor;

C_n = concentration of fission product of species n per unit weight of product;

i and p = initial and product streams, respectively;

X_n = fraction of radioactivity due to species n in initial feed stream;

(d.f.)n = individual fission-product decontamination factor of species n.

The equation above may be expended to read:

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$$D.F. = \frac{1}{\frac{X_1}{(d.f.)1} + \frac{X_2}{(d.f.)2} + \frac{X_3}{(d.f.)3} + \sum_4^n \frac{X_n}{(d.f.)n}} \quad \ldots\ldots(2)$$

where 1,2, and 3 refer to Ru, Zr.+ Nb, and Ce, respectively. The summation term in Equation (2) refers to all other fission products present in untreated dissolver solution. The discussion which follows assumes that the fraction of the total initial radioactivity of these remaining individual species is so small and the individual decontamination factor so large in the Redox process that the summation term is negligible in comparison to the first three terms in the denominator of Equation (2). The equation then reduces to :

$$D.F. = \frac{1}{\frac{X_1}{(d.f.)1} + \frac{X_2}{(d.f.)2} + \frac{X_3}{(d.f.)3}} \quad \ldots\ldots\ldots(3)$$

The relationship between beta decontamination factors may be plotted from Equation (3) with the use of the following average experimental data on IAF beta radiation spectra:(115)

Fractional Beta Radioactivity of IAF

X_1(Ru)	X_2(Zr + Nb)	X_3(Ce)
0.057	0.089	0.50

Two cases will be considered. Case I (for Pu) will assume that the over-all beta D. F. required for Pu is 10^7. The relationships are plotted in Figure IV-60 with various possible Ce decontamination factors as parameters. Case II (for U) will assume that the term $X_3/(d.f.)3$ for Ce is negligible in comparison with the remaining two terms in the denominator of Equation (3); i.e., Ce decontamination is adequate. The relationships are plotted in Figure IV-61 with various over-all uranium D. F.'s as parameters.

The use of these simple plots is illustrated by the following example. If the over-all beta D. F. for U is required to be 1×10^6 and the experimental beta decontamination factors from Ru and Zr + Nb are 10^4 and 10^6, respectively, Figure IV-61 shows that the Ru decontamination factor must be improved by a factor of about 6 in order to meet the required uranium purity. In addition, the plot shows that little or no improvement in uranium purity will be achieved by increasing the Zr + Nb beta decontamination factor above 10^6.

A similar set of plots may be constructed for gamma radiation decontamination factors from a knowledge of the fractional gamma radiation spectra of IAF solutions.

4.85 Effect of head-end treatment

The improvement in decontamination obtained by the volatilization of Ru from the dissolver solution, followed by Zr and Nb scavenging, may make the elimination of third solvent-extraction cycles for uranium and plutonium possible. A summary of S.P.R.U. run data(121) indicates that ozonolysis, nitrogen sparging, or steam sparging of permanganate-oxidized dissolver solution, followed by MnO_2 scavenging, are equally beneficial to total beta and gamma decontamination. Laboratory results at Hanford have shown that Ru decontamination factors of 20 or more should be consistently obtained by any of the above volatilization procedures. Additional gamma D. F.'s of 20 are obtained by Zr + Nb scavenging using either Super Filtrol or co-formed MnO_2. When MnO_2 is used as the scavenging agent a beta decontamination factor of the order of 2 is consistently encountered in scavenging due to Ru and/or Ce removal.(120)

5. Nitric Acid

5.1 Introduction

Nitric acid is present in varying amounts in both organic and aqueous phases throughout the process. Its distribution between the two phases is highly dependent upon the concentrations of $Al(NO_3)_3$ and $UO_2(NO_3)_2$, as well as the concentration of the acid itself. For a discussion of the role of nitric acid in the Redox process, see Section A.

5.2 Effect of salting agent

The effect of increasing aluminum nitrate concentration in the aqueous phase, at fixed nitric acid and uranyl nitrate concentrations is illustrated by curves 2, 4, and 8 of Figure IV-62. In general, an increase in aluminum nitrate concentration increases the distribution ratio of nitric acid in the organic phase; e.g., at 0.5 M $UO_2(NO_3)_2$, increasing the $Al(NO_3)_3$ concentration from 0.5 M to 1.0 M increases the HNO_3 E_a^o from 0.5 to 0.8.(194)

5.3 Effect of nitric acid concentration

In the absence of uranyl nitrate, the distribution ratio, E_a^o, of nitric acid increases linearly as the nitric acid concentration in the aqueous phase increases (curves 2, 4, and 8 of Figure IV-62).

The concentration of nitric acid in hexone which is in contact with an acid-deficient solution of aluminum nitrate may be calculated from the equation:(132)

$$\log_{10}(HNO_3)_{org.} = -0.74 + 0.4 \log_{10}(Al(NO_3)_3)_{aq.} - 0.92\ pH_{aq.},$$

where concentrations are in molarities. The equation is valid over a range of $Al(NO_3)_3$ concentrations from 1.0 to 1.5 M and a pH range from 0.6 to 2.0.

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When uranyl nitrate is present in the aqueous phase, the distribution ratio, E_a^o, of nitric acid decreases with increasing nitric acid concentration in the aqueous phase (curves 1,3,5,6, and 7 of Figure IV-62), at a rate which varies for different salt combinations.

5.4 Effect of uranium concentration

Increasing uranyl nitrate concentration in the aqueous phase increases the distribution of the nitric acid into the organic phase, as shown by curves 1, 2, 3, and 5 of Figure IV-62. At 0.0 M $Al(NO_3)_3$, an increase in uranium concentration in the aqueous phase from 0.5 M to 1.0 M increases the distribution ratio from 0.2 to 0.33.

5.5 Effect of temperature

An increase in temperature from 0°C. to 60°C. decreases the distribution ratio, E_a^o, of nitric acid from 0.085 to 0.058 as shown in Figure IV-63. The relationship between distribution coefficient and temperature is approximately linear in this temperature range.(156)

6. Others

6.1 Sulfamic acid

The distribution ratio, E_a^o, for sulfamic acid is given in the following table as a function of the concentration of the salting agent:(104)

Salting Agent	Distribution Ratio of Sulfamic Acid, G./L. Organic / G./L. Aqueous
1.0 M $Al(NO_3)_3$	0.0023
1.5 M $Al(NO_3)_3$	0.0037
8.0 M NH_4NO_3	0.0020

Aqueous phase: 0.3 M HNO_3, 0.2 M NH_2SO_3H.
Organic phase: Pretreated hexone, 0.3 M HNO_3.

6.2 Ferrous sulfamate

The distribution ratio, E_a^o, of ferrous sulfamate is about 2×10^{-4} between hexone and an aqueous phase containing 1.3 M $Al(NO_3)_3$, ~0.05 M HNO_3, and 0.04 M $Fe(NH_2SO_3)_2$. There is evidence that 0.01 M $UO_2(NO_3)_2$ in the aqueous phase increases this value about three-fold.(137)

6.3 Chromium

Chromium, as Cr(III), has an extremely small distribution ratio, E_a^o, which appears to be almost independent of chromium concentration and salting strength in the aqueous phase. The highest E_a^o value probably does not exceed 3×10^{-4} where pretreated hexone is employed. The presence of methyl isobutyl carbinol in the hexone, however, may increase this to 10^{-3}.(102)

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In the hexavalent state, i.e., in the form of $Cr_2O_7^=$, chromium is quite extractable into the hexone phase. The distribution ratio, E_a^o, of this ion increases with the acid concentration in the aqueous phase as shown in the following table:(102)

pH	Distribution Ratio of $Cr_2O_7^=$, G./L. Organic / G./L. Aqueous
0.17	0.170
0.42	0.083
0.77	0.080
1.70	0.011
2.61	0.0058
8.50	0.0001

The distribution ratio for Cr(VI) appears to be little affected by either salting agent concentration or length of contact time.

6.4 Iron

The distribution ratio of iron is dependent upon the oxidation state. From an aqueous phase containing 8 M NH_4NO_3 and 0.2 M HNO_3 the distribution ratio, E_a^o, of ferric ion is less than 5×10^{-4}, as compared to 4×10^{-3} for ferrous ion.(83)

6.5 Aluminum

Equal volumes of 1.3 M $Al(NO_3)_3$ and hexone were equilibrated and analyzed. The organic phase was found to contain 1.1 mg. $Al(NO_3)_3$ per liter. The distribution ratio calculated from this datum is about 2×10^{-6}.(161)

6.6 Sodium

The distribution ratio, E_a^g, of sodium is about 2×10^{-2} in the following system:(209)

Aqueous: 1.3 M $Al(NO_3)_3$, 0.05 M $Fe(NH_4)_2SO_4$, 0.1 M HSO_3NH_2, 0.2 M $NaNO_3$ -- corresponding to 2DS.

Organic: 0.476 M $UO_2(NO_3)_2$, 0.017 M HNO_3 in water-saturated hexone -- corresponding to 2DU.

Volume ratio: 2DS:2DU: :1:4.2.

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(187) HW-18415 Decontamination from Ruthenium by Ozonization in the Redox Process. C. F. Callis, L. H. Clark, and K. M. Harmon. 7-25-50.

(188) HW-18773 Equilibrium Relationships for the IC Column System. F. M. Empson et al. To be issued.

(189) HW-18880 Chemical Research Section Report -- August, 1950. O. F. Hill. 9-19-50.

(190) HW-19047 Plutonium Extraction Stage and Transfer Unit Requirements -- Redox Second and Third Plutonium Cycles. R. B. Lemon. 10-10-50.

(191) HW-19096 The Reactions of Hexone in the Redox Process. L. L. Burger. 9-1-50.

(191a) HW-19156 Specifications, Acceptance and Sampling Procedures for Essential Materials. E. W. Rebol. May, 1951. P. 93.

(192) HW-19303 Physical Properties of the System: Uranyl Nitrate-Aluminum Nitrate-Nitric Acid-Water-Hexone. C. Groot et al. 12-1-50.

(193) HW-19678 Redox Production Plant Chemical Flowsheet, HW No. 4. R. J. Sloat. 12-20-50.

(194) HW-19949 Properties of the System: $UO_2(NO_3)_2$-$Al(NO_3)_3$-HNO_3-(or NaOH)-H_2O-Hexone, Part VII -- Distribution Coefficients of Uranyl Nitrate and Nitric Acid. L. L. Burger, I. M. Rehn, and C. M. Slansky. To be issued.

(195) HW-20287 Decontamination of Redox Feed Solutions by Super Filtrol Scavenging. W. E. Roake and H. G. Hicks. 9-1-50.

(196) HW-20366 Physical Properties of Redox Composite Aqueous Waste. M. H. Curtis. To be issued.

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(198) HW-20863 Chemical Research Section Quarterly Report, January-March, 1951. O. F. Hill and F. J. Leitz. 4-16-51.

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(204) Informal communication. C. M. Slansky, Hanford Works.

(205) Informal communication. A. W. Allen, Hanford Works.

(206) Informal communication. Communication on '25' Process. D. G. Reid, Oak Ridge.

(207) Analytical Procedure Code No. RDT-1, Settling Time -- Redox Methods, Hanford Works. (See also Chapter XX).

(208) Unpublished data. Chemical Research Section, Hanford Works.

(209) Unpublished data. Chemical Development Section, Hanford Works.

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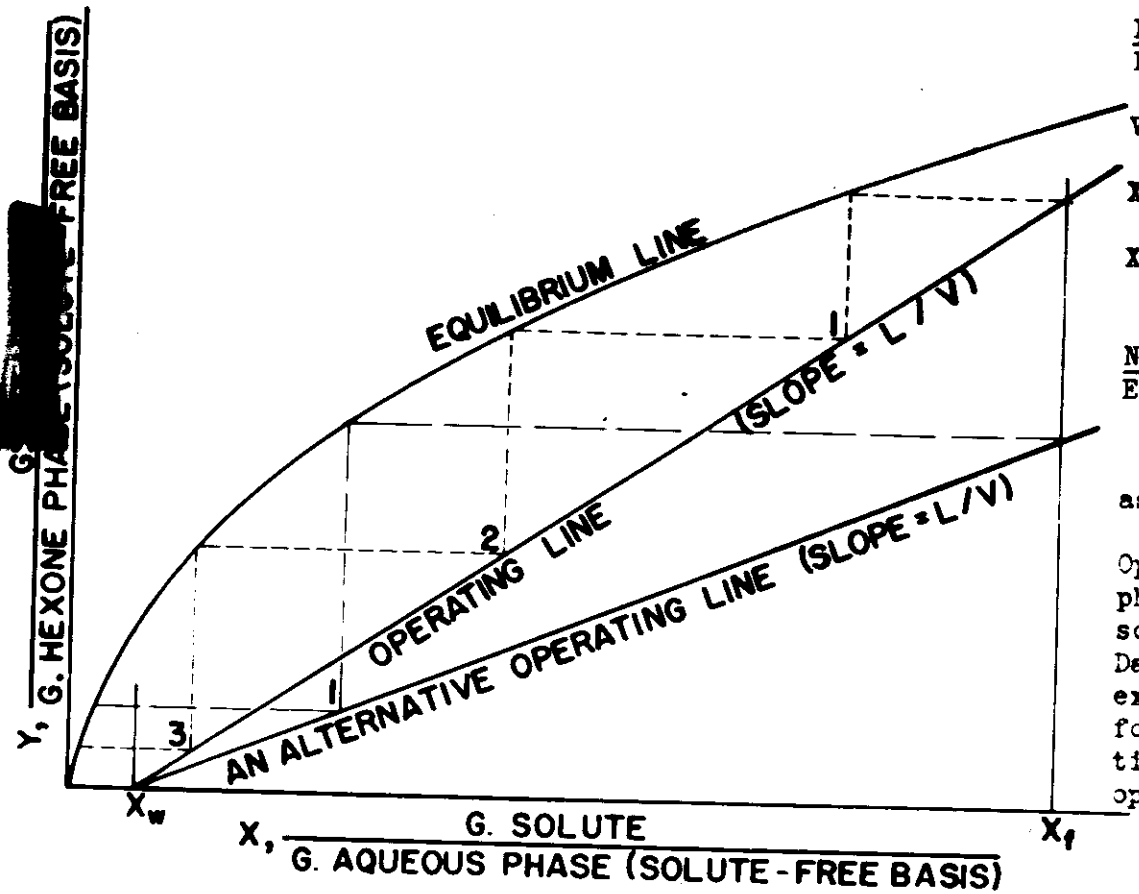
FIGURE IV - 1

EFFECT OF L/V RATIO ON STAGE REQUIREMENTS FOR EXTRACTION

(TRANSFER FROM AQUEOUS TO HEXONE PHASE)



LEGEND:

L = Weight of solute-free aqueous phase per unit time

V = Weight of solute-free hexone phase per unit time

X_f = Concentration of solute in aqueous feed stream

X_w = Concentration of solute in aqueous waste stream

NOTES:

Equation for operating lines is:

$$Y = \frac{L}{V}X - \frac{L}{V}X_w ,$$

assuming no solute in entering hexone.

Operating lines represent different phase ratios for reducing the aqueous solute concentration from X_f to X_w. Dashed lines indicate the step-off of extraction stages required: 3.5 stages for the higher aqueous to organic ratio, 1.8 stages for the alternative operating line.

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218

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TABLE IV-2

COMPARISON OF [redacted] FLOWSHEETS
[redacted] COMPOSITIONS

	[redacted] June, 1948 Flowsheet	ORNL (Acid-Deficient) June, 1949 Flowsheet *	HW (Hytrid) Flowsheet No. 4
IAF, Aqueous:			
Relative flow rate	100	100	100
Density, g./ml.	1.654	1.6	1.68
$UO_2(NO_3)_2.6H_2O$, M	2.0	2.0	2.0
HNO_3, M	0.3	-0.2	-0.2
$Al(NO_3)_3.9H_2O$, M	---	---	---
$Na_2Cr_2O_7.?\ H_2O$, M	0.1	0.1	0.1
$NaNO_3$, M	---	0.38	0.38
IAS, Aqueous:			
Relative flow rate	100	100	100
Density, g./ml.	1.190	1.3	1.28
HNO_3, M	---	- 0.2	-0.2
$Al(NO_3)_3.9H_2O$, M	1.3	2.0	1.8
$Na_2Cr_2O_7.2H_2O$, M	---	0.01	0.01
$NaNO_3$, M	---	0.2	0.2
IAX, Hexone:			
Relative flow rate	400	400	400
Density, g./ml.	0.819	0.8	0.81
HNO_3, M	0.5	<0.01	0.2
IAW, Aqueous:			
Relative flow rate	178	180	180
Density, g./ml.	1.144	1.18	1.18
Uranium, % of IAF	0.1	0.1	0.2
Plutonium, % of IAF	0.1	0.1	0.2
HNO_3, M	0.8	-0.3	0.18
$Al(NO_3)_3.9H_2O$, M	0.73	1.08	0.98
$Na_2Cr_2O_7.2H_2O$, M	0.056	0.06	0.05
$NaNO_3$, M	---	0.11	0.32
IAF-IBF, Hexone:			
Relative flow rate	420	420	420
Density, g./ml.	0.972	0.97	0.97
Uranium, % of IAF	99.9	99.9	99.8
Plutonium, % of IAF	99.9	99.9	99.8
$UO_2(NO_3)_2.6H_2O$, M	0.476	0.476	0.476
HNO_3, M	0.21	0.05	0.017
IBS, Hexone:			
Relative flow rate	200	200	200
Density, g./ml.	0.800	0.80	0.80
HNO_3, M	0.01	<0.01	0.05
IBX, Aqueous:			
Relative flow rate	40	40	40
Density, g./ml.	1.197	1.2	1.21
HNO_3, M	---	0.05	0.05
$Al(NO_3)_3.9H_2O$, M	1.28	1.3	1.3
Fe^{++}, M	0.05	0.05	0.05
$NH_2SO_3^-$, M	0.10	0.10	0.10
IBF, Aqueous:			
Relative flow rate	40.4	40.4	40.4
Density, g./ml.	1.193	1.19	1.19
Uranium, % of IAF	2.5×10^{-5}	2.5×10^{-5}	2.5×10^{-5}
Plutonium, % of IAF	99.8	99.8	99.6
HNO_3, M	0.01	---	0.021
$Al(NO_3)_3.9H_2O$, M	1.277	1.297	1.297
Fe^{++}, M	0.05	0.05	0.05
$NH_2SO_3^-$, M	0.10	0.10	0.10
IBU-ICF, Hexone:			
Relative flow rate	620	620	620
Density, g./ml.	0.816	0.91	0.91
Uranium, % of IAF	99.9	99.9	99.8
Plutonium, % of IAF	0.1	0.1	0.2
$UO_2(NO_3)_2.6H_2O$, M	0.323	0.323	0.323
HNO_3, M	0.145	0.04	0.029
ICX, Aqueous:			
Relative flow rate	200	200	200
Density, g./ml.	1.000	1.00	1.00
HNO_3, M	0.1	0.1	0 to 0.04
ICW, Hexone:			
Relative flow rate	588	580	580
Density, g./ml.	0.800	0.80	0.80
Uranium, % of IAF	0.01	0.01	0.05
Plutonium, % of IAF	---	---	---
HNO_3, M	0.01	---	---
ICU, Aqueous:			
Relative flow rate	230	240	240
Density, g./ml.	1.892	1.85	1.85
Uranium, % of IAF	99.9	99.9	99.75
Plutonium, % of IAF	0.1	0.1	0.2
$UO_2(NO_3)_2.6H_2O$, M	0.87	0.835	0.835
HNO_3, M	[redacted]	0.18	0.075

*Also known as ORNL No. 1 Flowsheet. [redacted]

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320

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TABLE IV-3

PHYSICAL PROPERTIES OF HEXONE

PROPERTY		
Formula		[redacted]$O \cdot CH_2 \cdot CH(CH_3)_2$; $C_6H_{12}O$
Nomenclature		[redacted]-methyl-2-pentanone; methyl isobutyl ketone; hexone
Molecular Weight		100.16
Vapor Pressure,	0°C.	4.42 mm. Hg.
	30°C.	26.19 mm. Hg
	100°C.	468.3 mm. Hg
	115.89°C.	760.0 mm. Hg
		$\log_{10} P_{mm} = 23.66786 - \frac{2790.4}{T} - 5.2566 \log_{10} T$ ($T = t°C. + 273.15$)
Boiling Point		115.9°C. at 760 mm. Hg (For a list of reported values see KAPL-8)
Change of Boiling Point with Pressure		$dt/dp = 0.046°C./mm.$ Hg
Freezing Point		-80.26°C.
Density,	0°C.	0.8186 g./cu. cm.
	20°C.	0.8004 g./cu. cm.
	30°C.	0.7912 g./cu. cm.
Change in Density with Temperature		$d^t = 0.8186 - 9.00 \times 10^{-4} t - 4.5 \times 10^{-7} t^2$ d = density (g./cu. cm.) t = temperature (°C.)
Cubical Coefficient of Expansion		0.00118/°C., 20°C. to 30°C.
Index of Refraction, n_D^{20}		1.3958
Surface Tension, 25°C.		25.4 dynes/cm.
Parachor		276.5
Dielectric Constant		13.11
Specific Conductance		4.71×10^{-8} mhos/cm.
Viscosity,	0°C.	0.769 centipoises
	20°C.	0.585 centipoises
	25°C.	0.546 centipoises
	30°C.	0.522 centipoises
Latent Heat of Vaporization		86.5 cal./g.
Specific Heat,	20°C.	0.459 cal./g.
Heat of Combustion		8910 cal./g.
Flash Point, Tag Open Cup		81°F.
Tag Closed Cup		60°F.
Ignition Temperature		495°C.
Limits of Flammability in Air, (Per Cent by Volume)	Upper	[redacted] at 100°C.
	Lower	[redacted] at 50°C.

See SC-48-1 for optical properties such as infrared and ultraviolet absorption and X-ray and Raman spectra.

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222

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FIGURE IV-4

MUTUAL SOLUBILITIES OF HEXONE AND WATER

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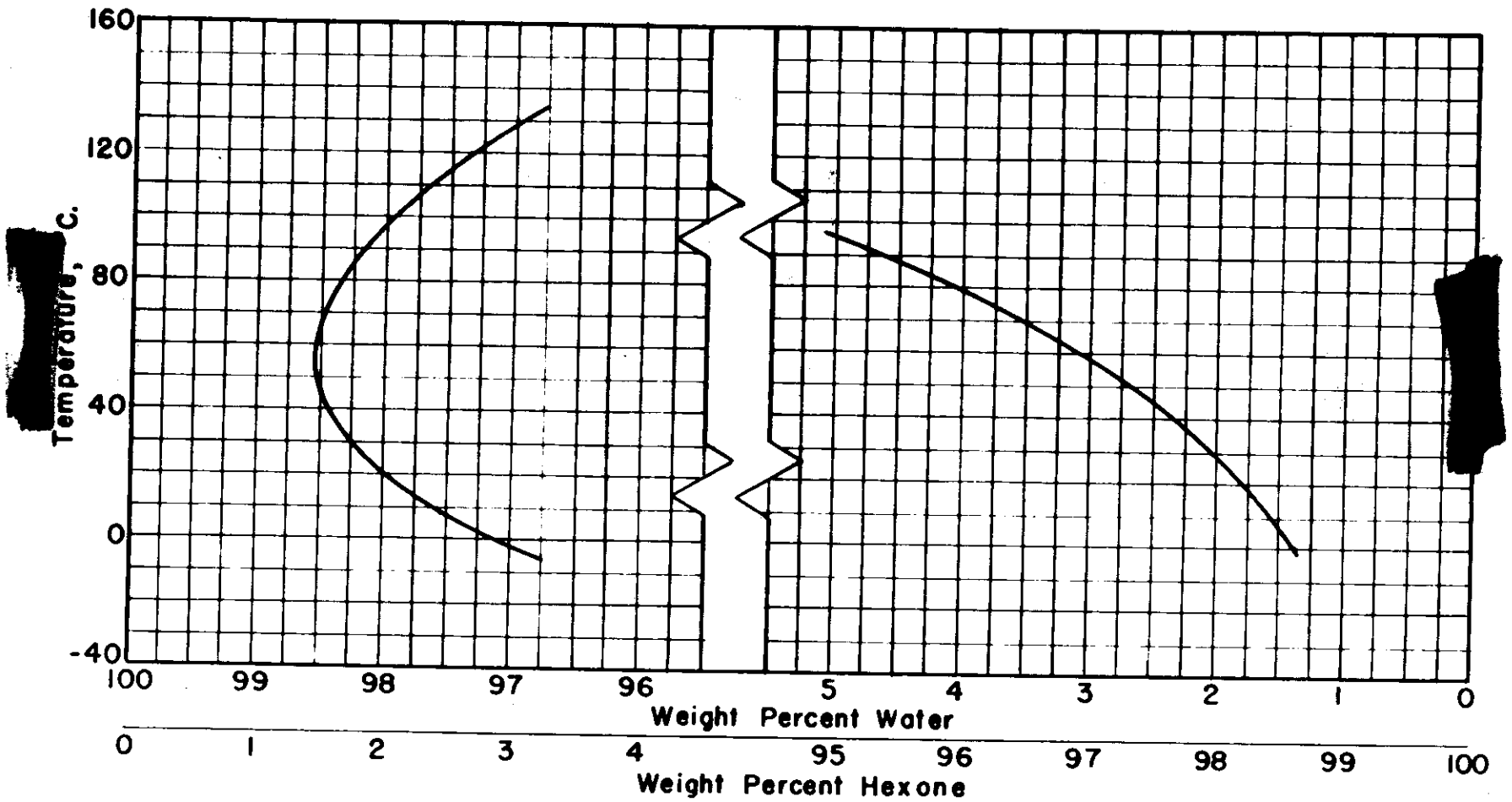

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TABLE IV-5A

LIQUID-V[redacted]A

HEXONE-WATER SYSTEM AT 760 Mm.

Vapor Temperature, °C.	Liquid Composition, % Hexone		Vapor Composition, % Hexone		Relative Volatility (Hexone to Water)	
	Wt.%	Mole %	Wt.%	Mole %	Water Layer	Hexone Layer
97.5	0.201	0.036	34.1	8.52	258	---
94.1	0.656	0.119	62.0	22.7	247	---
92.8	0.801	0.145	69.2	28.8	278	---
87.9	1.08	0.196	75.6	35.8	284	---
87.9	4.00	0.744	75.6	35.8	284	0.0669
87.9	95.0	77.4	75.6	35.8	284	0.0669
87.9	97.9	89.3	75.6	35.8	---	0.0669
90.0	98.4	91.6	76.5	36.9	---	0.0537
93.5	99.0	94.7	77.7	38.6	---	0.0352
107.6	99.82	99.0	89.8	61.3	---	0.0160
110.4	99.85	99.2	92.0	67.4	---	0.0167
114.0	99.88	99.3	98.0	89.7	---	0.0614

TABLE IV-5B

AZEOTROPE DATA

HEXONE-WATER SYSTEM

PRESSURE - TEMPERATURE - VAPOR COMPOSITION

Pressure, Mm. Hg	Temperature, °C.	Wt. % Hexone
27	19.8	81.2
27	20.4	81.1
45	25.9	81.0
49	26.9	81.1
89	38.4	79.3
102	--	80.4
108	42.3	79.6
110	42.8	79.7
111	42.9	80.1
197	55.1	79.6
207	56.0	78.5
382	70.3	77.7
384	70.4	77.9
752	87.5	75.9
752	87.5	76.1
752	87.5	76.7
760	87.93	75.7

$\log_{10} P (H_2O) = 8.7942$ [redacted] Hexone) $= 7.9649 - \frac{1991.1}{T}$

P = partial pressure in mm. Hg. T = temperature in degrees Kelvin.

Latent Heat of Vaporization: 9500 cal./g. of azeotrope (calculated).

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FIGU[redacted]

EQUIVALENT CONDUCTANCE OF $UO_2(NO_3)_2$ AND HNO_3 IN HEXONE AT 25° C.

SOURCE OF DATA: UNPUBLISHED WORK OF CHEMICAL RESEARCH SECTION

H_2O present in less than saturation quantities

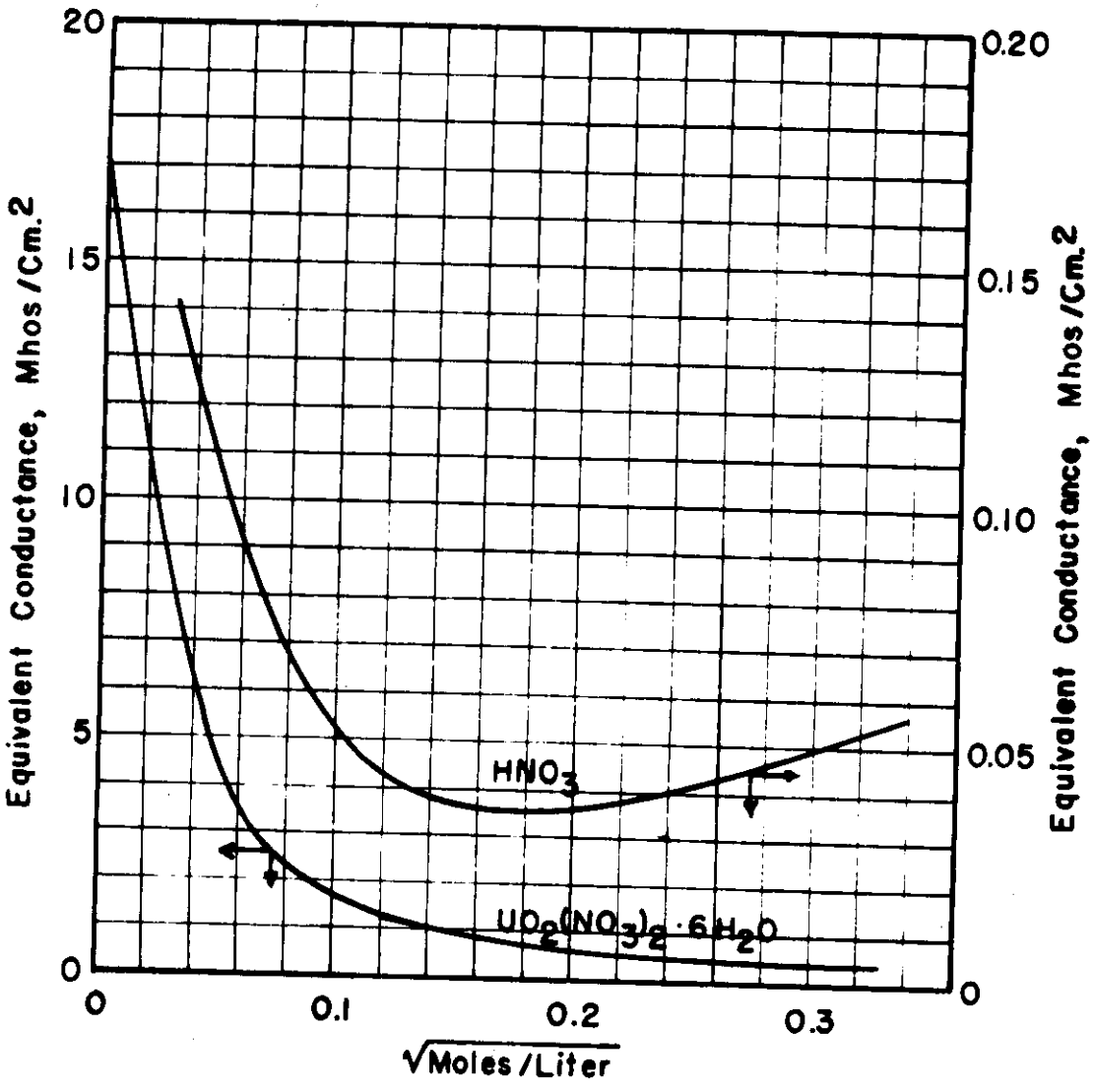

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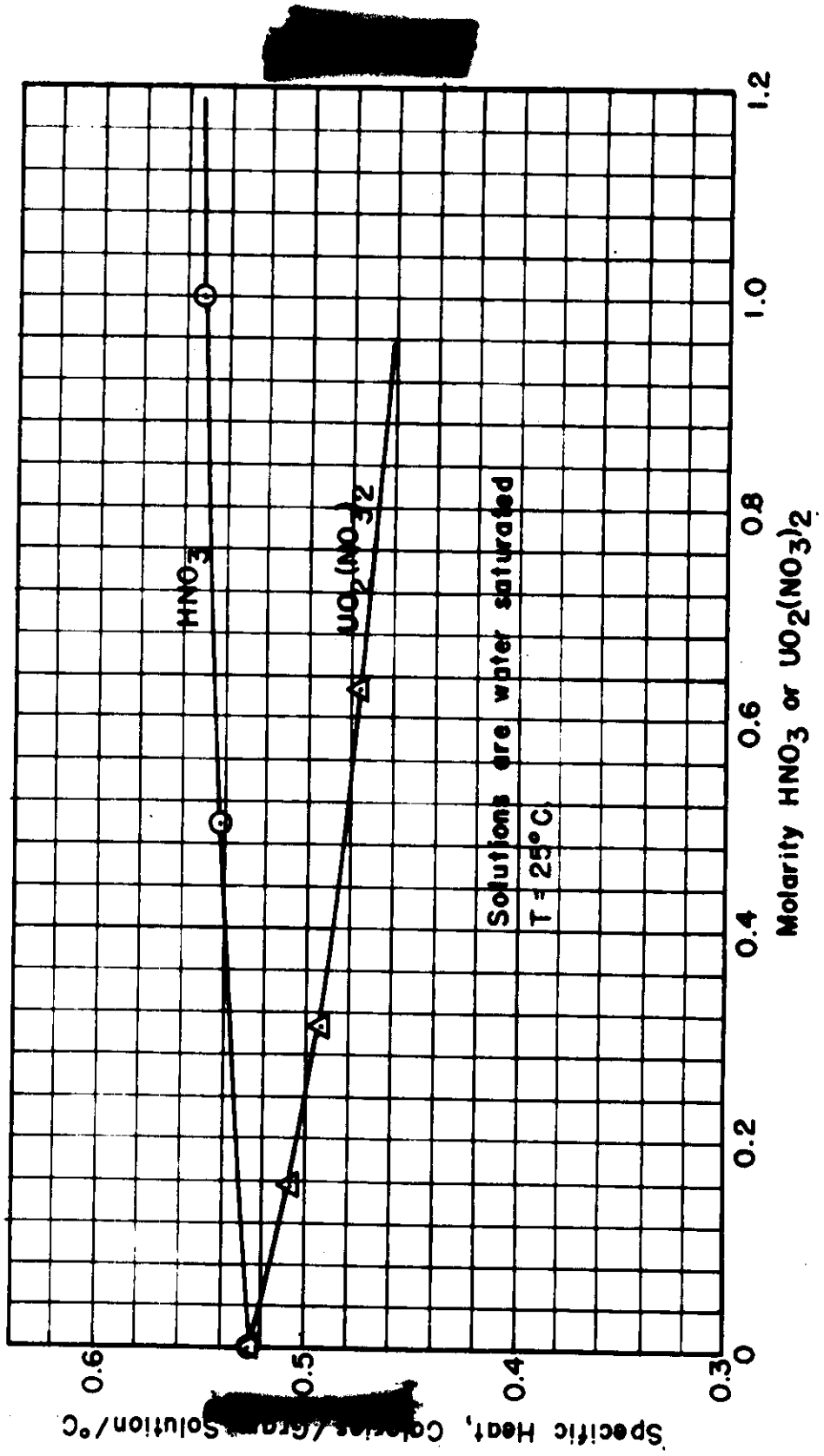
FIGURE IV-7

SPECIFIC HEATS OF SOLUTIONS IN HEXONE

SOURCE OF DATA: HW-11841



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SOLUBILITIES IN THE SYSTEM HEXONE-HNO_3-H_2O AT 25° C.

SOURCE OF DATA: CC-2394

In the portion of the diagram below the saturation curve the mixture separates into two liquid phases. The two points of contact between a tie line and the saturation curve indicate the compositions of two phases in equilibrium.

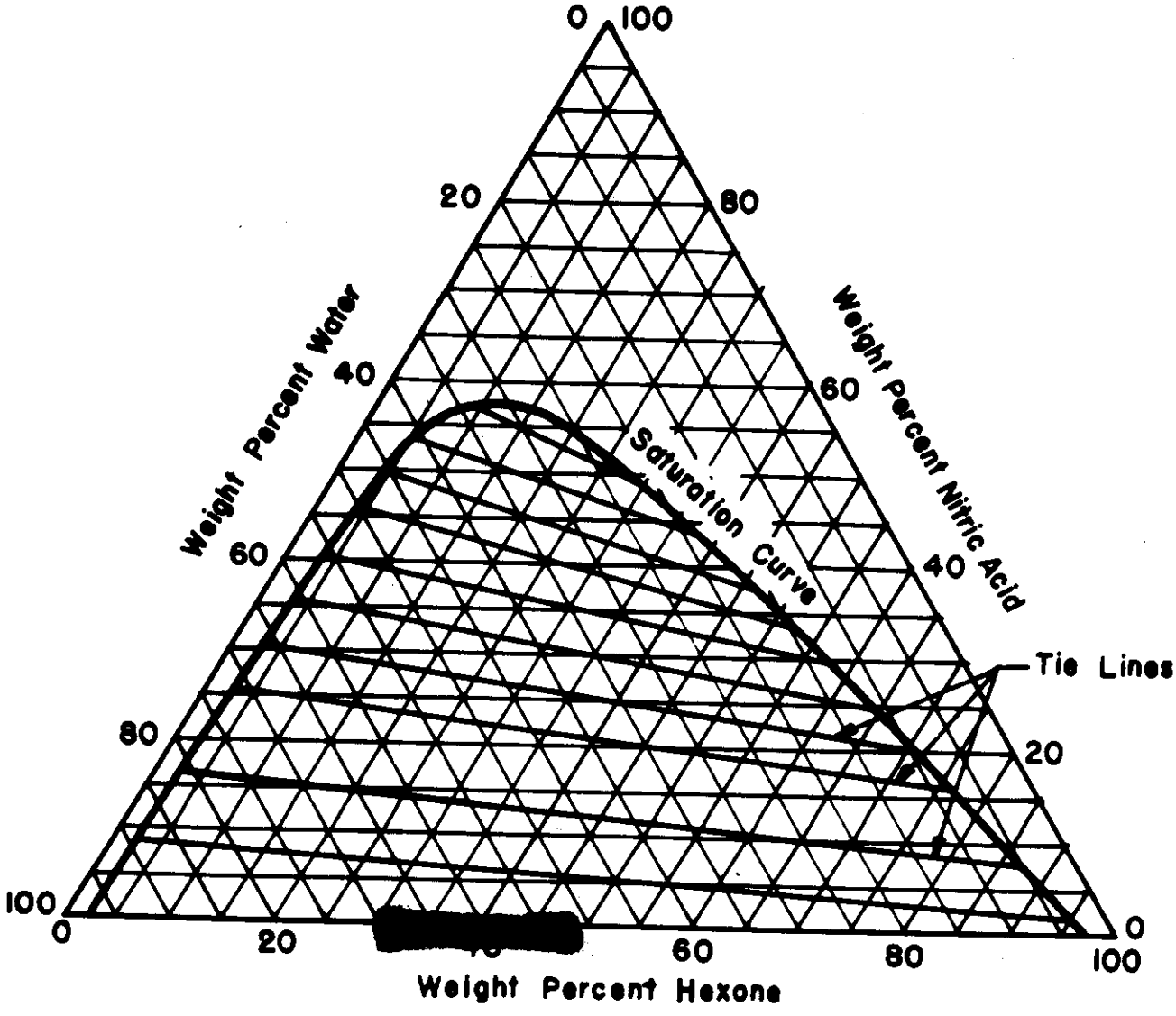

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FIGURE IV-9

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DENSITY OF SOLUTIONS OF HNO_3 IN HEXONE AT 25°C.

SOURCE OF DATA: CC-2394

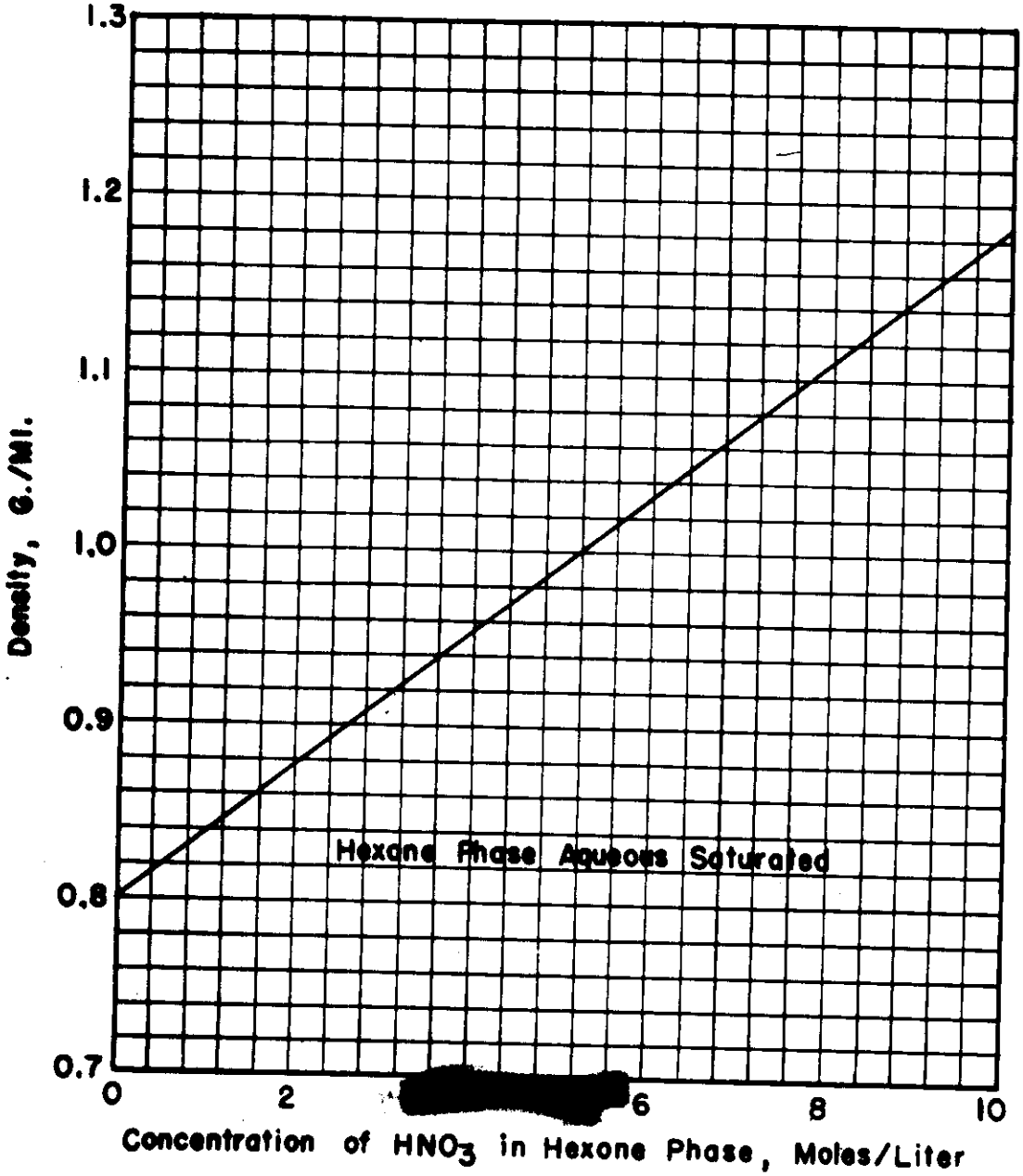

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FIGURE IV-10

TEMPERATURE–COMPOSITION PHASE DIAGRAM

SYSTEM: $Al(NO_3)_3$–HNO_3–H_2O

SOURCE OF DATA: SEIDELL, PP. 91-93

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FIGURE IV-11

[redacted] SOLUBILITY OF $Al(NO_3)_3$ IN NITRIC ACID

SOURCE OF DATA: SEIDELL, P. 92

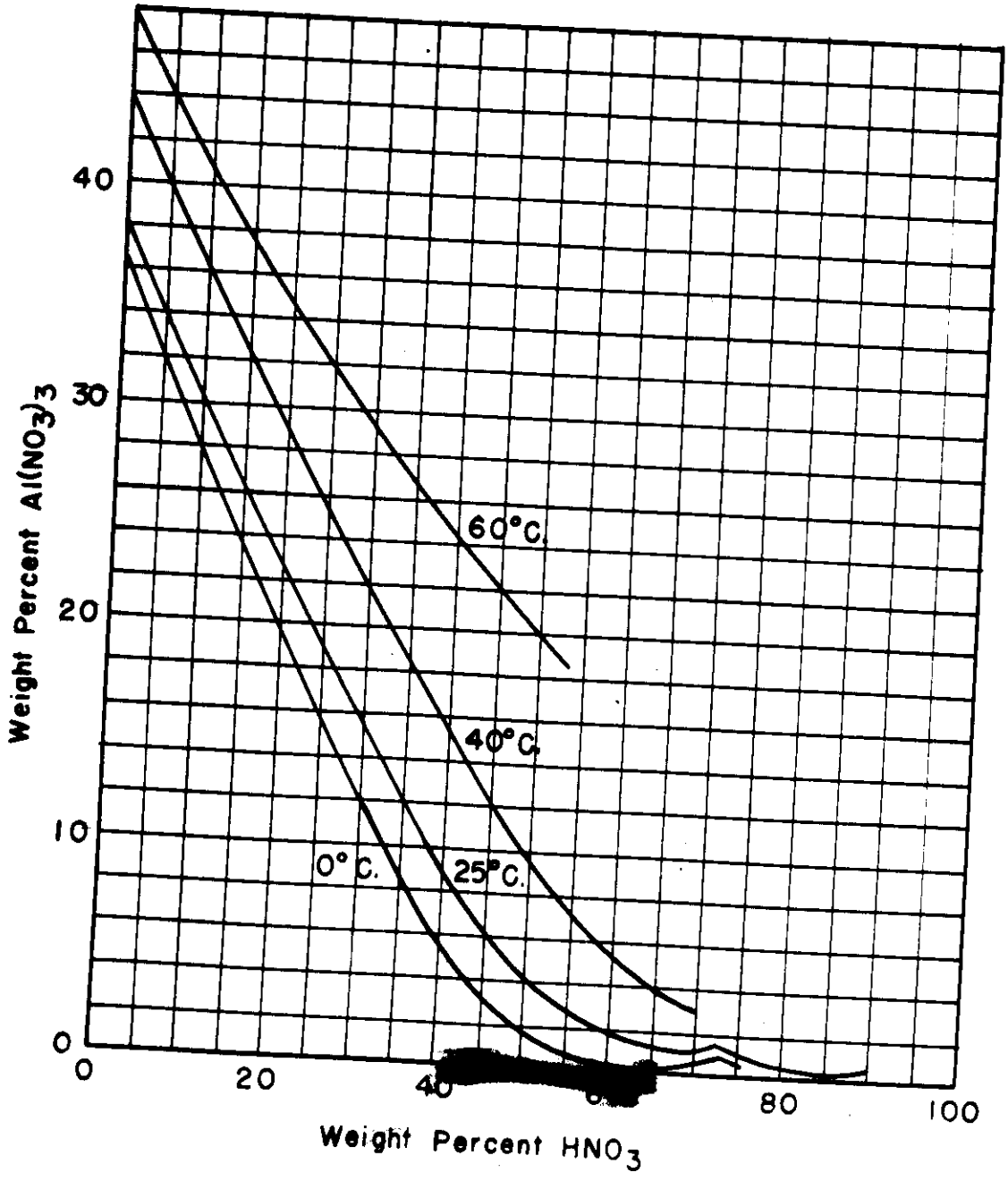

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FIGURE IV-12
FREEZING POINTS AND SOLUBILITY
COMPOSITE AQUEOUS WASTES

SOURCE OF DATA: HW-20366

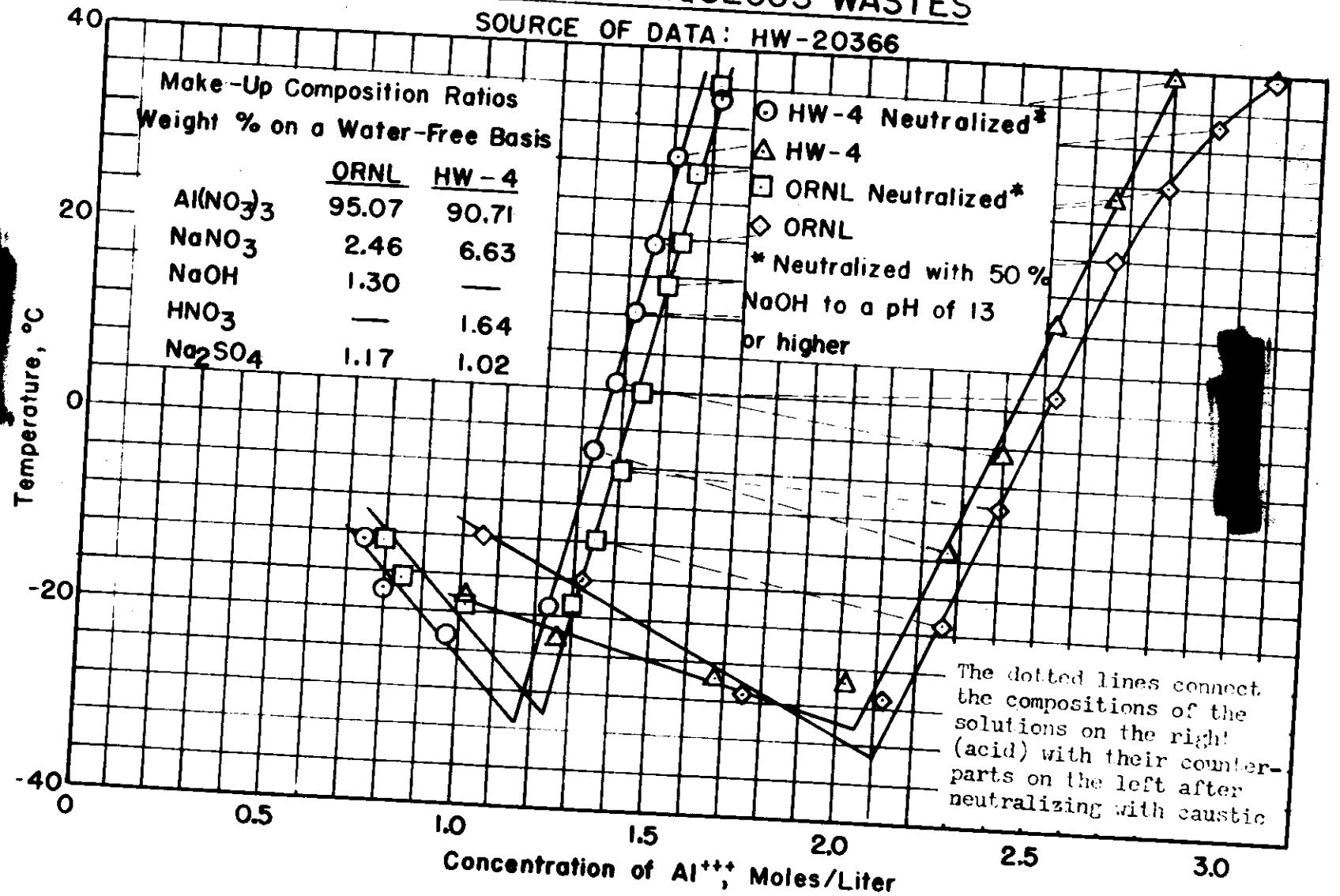

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FIGURE IV-12

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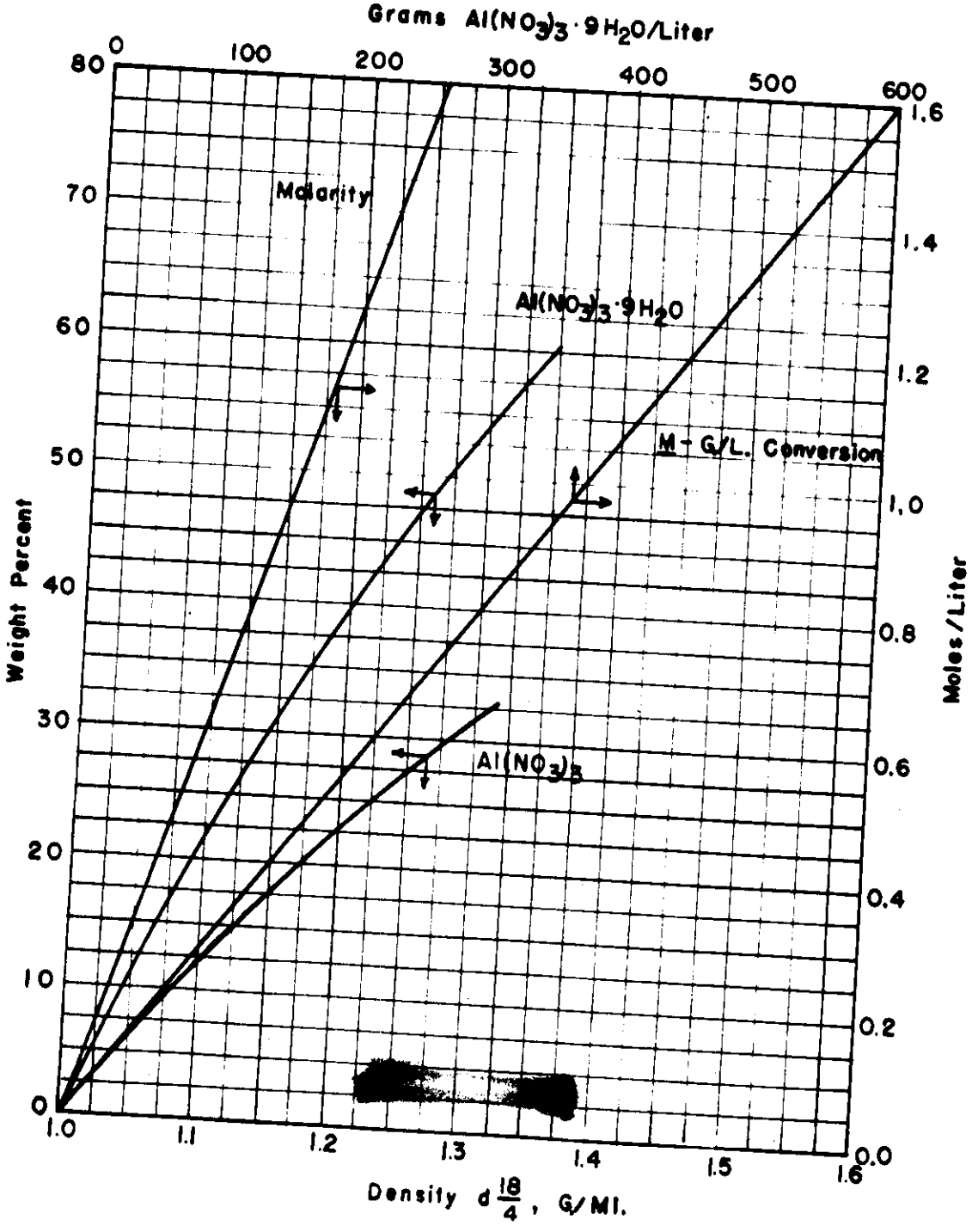
FIGURE IV-13

AQUEOUS ALUMINUM NITRATE SOLUTIONS

DENSITY AND CONCENTRATION CONVERSION CURVES

SOURCE OF DATA: CHEMICAL RUBBER HANDBOOK, P. 1653 (1947)



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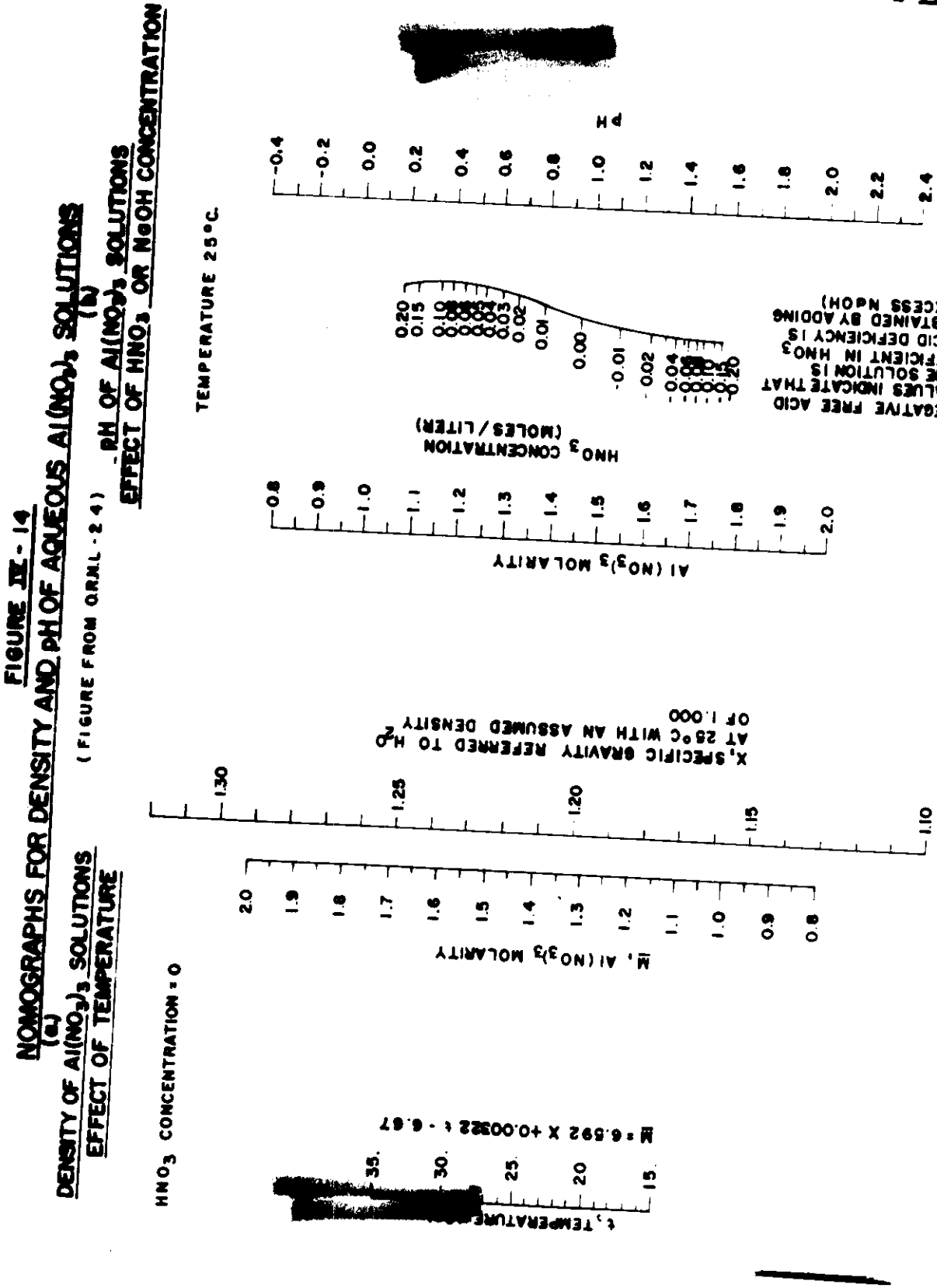

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FIGURE IV-15

DENSITY (25°C) OF AQUEOUS SOLUTIONS OF $UO_2(NO_3)_2$-$Al(NO_3)_3$-HNO_3

SOURCE OF DATA: HW-11276

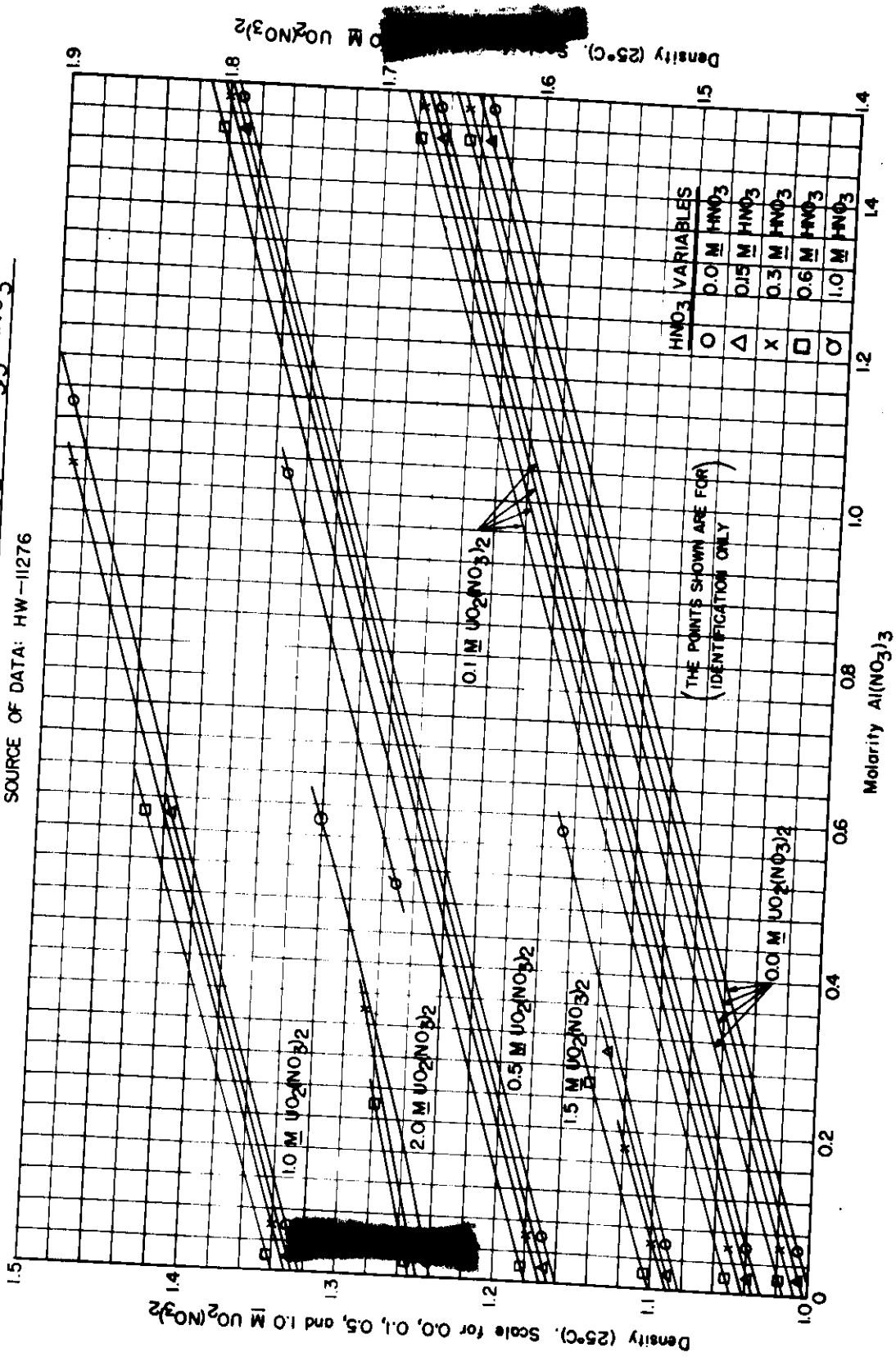

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TABLE IV- 16

SOURCE OF DATA: HW-11270

(A) CONCENTRATION COEFFICIENTS OF THE DENSITY EQUATION FOR REDOX AQUEOUS SOLUTIONS AT 25°C.

$$d^{25} = A + B\,\underline{M}_{UO_2(NO_3)_2} + [redacted]\,\underline{M}_{NaOH} + 0.198\,\underline{M}_{Na_2Cr_2O_7} + 0.051\,\underline{M}_{NaNO_3} + 0.172\,\underline{M}_{Fe(NH_2SO_3)_2}$$

Solution	Streams to which Applicable	A	B	C	D	Statistical * Error, σ_E
Aqueous (Hexone-Free)	1AF, 2EF, 3DF 1AS, 2DS, 3DS 1BX, 2AS, 2AF 3AS	1.0012	0.3177	0.03096	0.1553	0.0032
Aqueous (Hexone-Sat'd.)	1CU, 2EU, 3EU 1AW, 2DW, 3DW 2AW, 3AW, 3AF	0.9958	0.3164	0.0298	0.1600	0.0026

d = density in g./cu.cm.

(B) TEMPERATURE COEFFICIENTS FOR THE DENSITY OF REDOX SOLUTIONS

Aqueous Solutions (Hexone-Free)	$d^t = 1.0125\ d^{25} + 0.000145\ t - 0.000500\ t\ d^{25} - 0.0036$
Aqueous Solutions (Hexone-Saturated)	$d^t = 1.0123\ d^{25} + 0.000159\ t - 0.000491\ t\ d^{25} - 0.0040$

d = density in g./cu.cm.; t = temperature in °C.

(C) CONCENTRATION COEFFICIENTS OF THE VISCOSITY EQUATION FOR REDOX SOLUTIONS AT 25°C.

$$\log \eta = A + B\,\underline{M}_{UO_2(NO_3)_2} + C\,\underline{M}^2_{UO_2(NO_3)_2} + D\,\underline{M}_{Al(NO_3)_3} + E\,\underline{M}^2_{Al(NO_3)_3} + F\,\underline{M}_{UO_2(NO_3)_2}\,\underline{M}_{Al(NO_3)_3} + \left[G + H\,\underline{M}_{UO_2(NO_3)_2}\right]\underline{M}_{HNO_3} + \left[I + J\,\underline{M}_{UO_2(NO_3)_2}\right]\underline{M}_{NaOH} + X^{(a)}$$

η = viscosity in millipoises

Solution	A	B	C	D	E	F	G	H	I(b)	J(b)	Statistical* Error, σ_E
Aqueous (Hexone-Free)	0.9527	0.2426	0.01003	0.2660	0.0766	0.0554	0.0089	-0.0023	-0.047	0.040	0.004
Aqueous (Hexone-Sat'd)	0.969	0.241	0.0164	0.296	0.0507	0.0408	0.0077	0	-0.047	0.040	0.007

(a) Other constituents (X):

$Na_2Cr_2O_7$, 0.13 $\underline{M}_{Na_2Cr_2O_7}$

$Fe(SO_3NH_2)_2$, 0.29 $\underline{M}_{Fe(SO_3NH_2)_2}$

$NaNO_3$, $\left[0.025 + 0.030\,\underline{M}_{Al(NO_3)_3} + 0.015\,\underline{M}_{UO_2(NO_3)_2} + 0.005\,\underline{M}_{HNO_3} \pm 0.005\right]\underline{M}_{NaNO_3}$.

(b) For acid-deficient systems, G and H are replaced by I and J, respectively.

(D) TEMPERATURE COEFFICIENTS OF VISCOSITY FOR REDOX SOLUTIONS

$$\frac{d(\log \eta)}{d(1/T)} = 728.4 - 14.4\,\underline{M}_{UO_2(NO_3)_2} + 40.7\,\underline{M}^2_{UO_2(NO_3)_2} - 61.2\,\underline{M}_{Al(NO_3)_3} + 83.2\,\underline{M}^2_{Al(NO_3)_3} + 87.0\,\underline{M}_{UO_2(NO_3)_2}\,\underline{M}_{Al(NO_3)_3} - 34.1\,\underline{M}_{HNO_3}$$

η = viscosity in millipoises, T = temperature in °K.

Note:

1. Concentration limits in hexone-free solutions [redacted]

$\underline{UO_2(NO_3)_2}$ 2 M; $\underline{HNO_3}$ 1 M; $\underline{Al(NO_3)_3}$ 1.5 M; $\underline{NaNO_3}$ 2 M; $\underline{NaOH}$ 0.2 N; $\underline{Na_2Cr_2O_7}$ 0.1 M; $\underline{Fe(NH_2SO_3)_2}$ 0.1 M

2. Concentration limits in hexone-saturated solutions

$\underline{UO_2(NO_3)_2}$ 2 M; $\underline{HNO_3}$ 1 M; $\underline{Al(NO_3)_3}$ 1.5 M

* 80% of the experimental values fall within $\pm \sigma_E$

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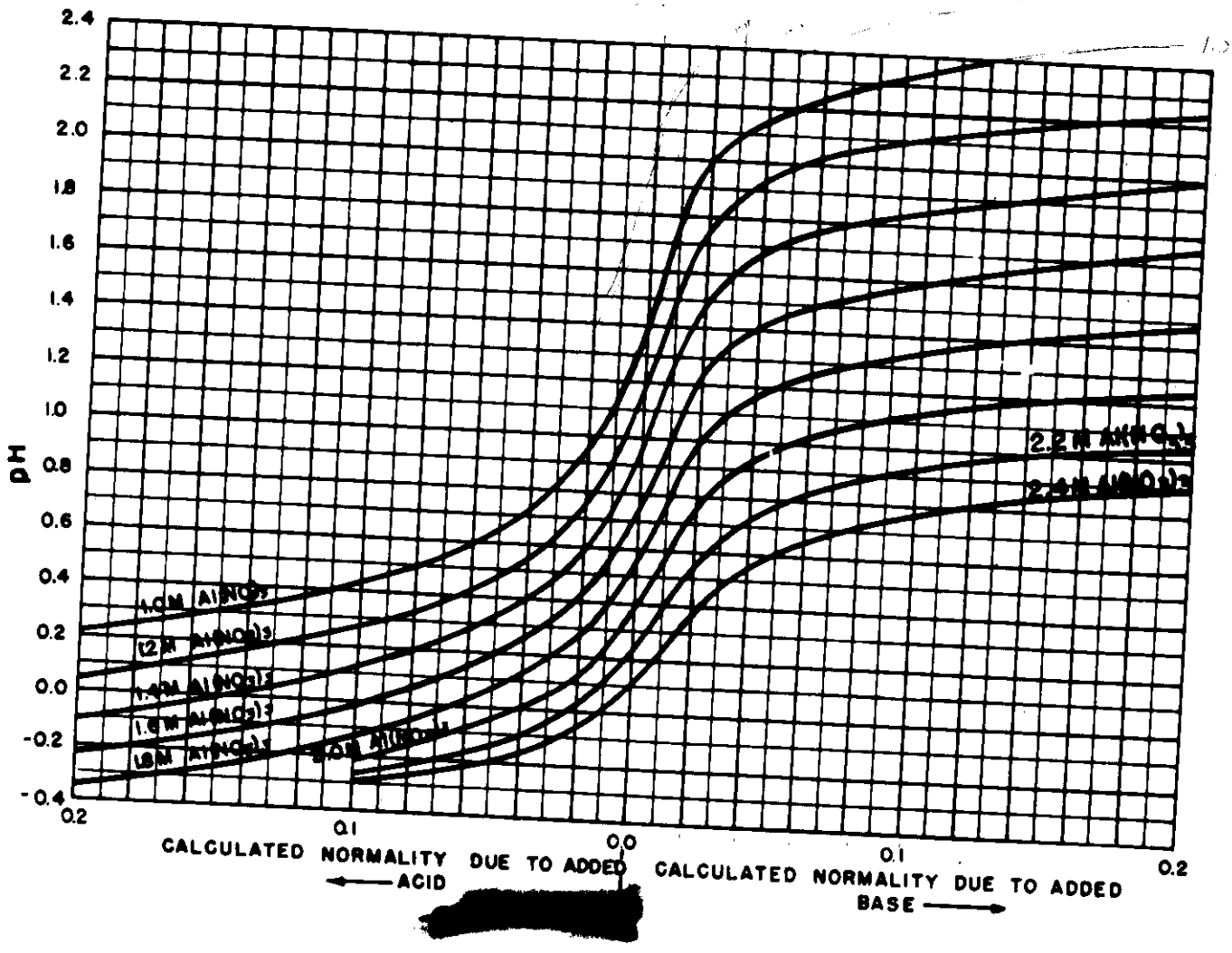
FIGURE IV-17

pH OF ALUMINUM NITRATE SOLUTION

SOURCE OF DATA: ORNL-24



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MELTING POINTS

$UO_2(NO_3)_2 - HNO_3 - Al(NO_3)_3 - H_2O$ SYSTEMS

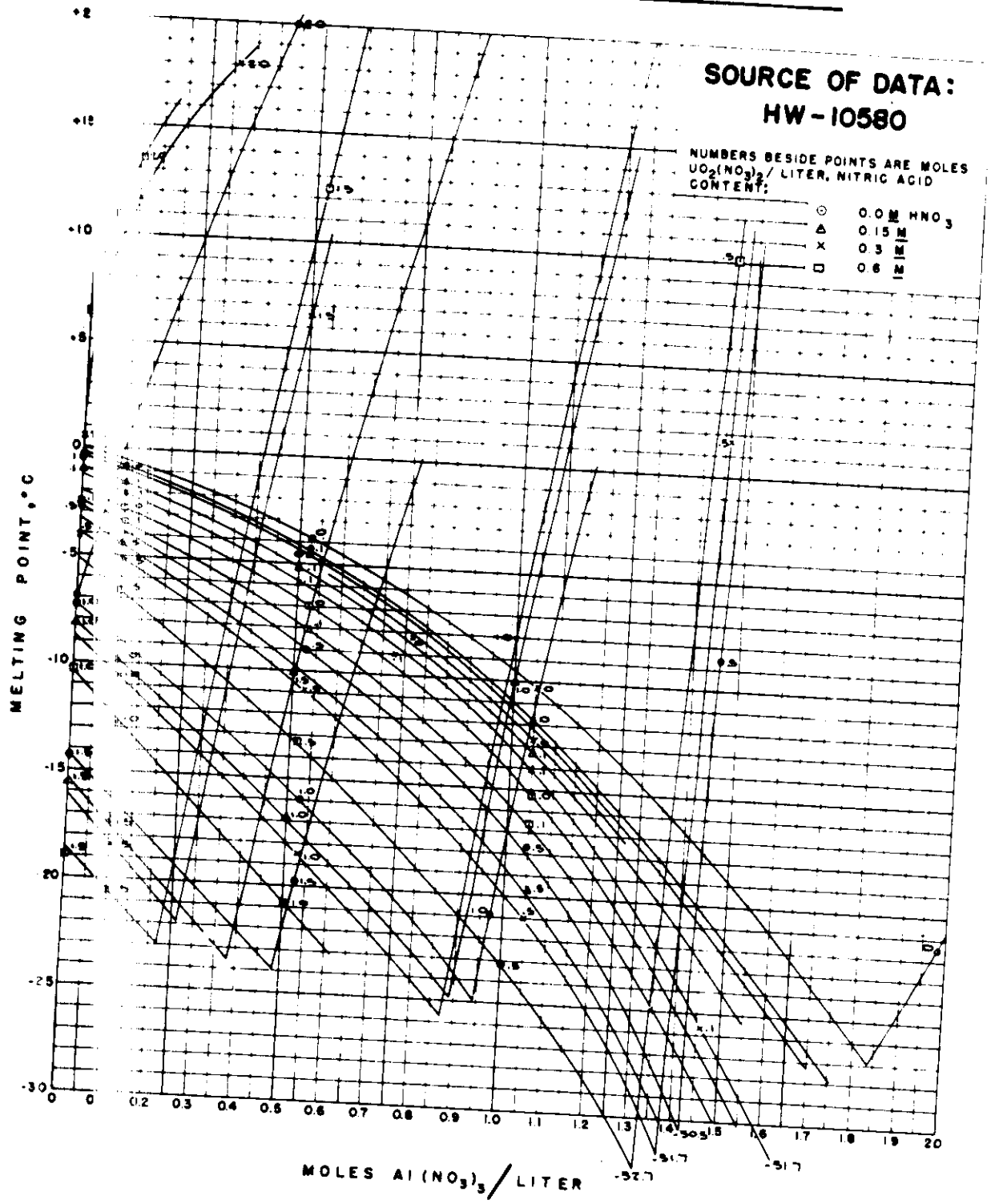

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FIGURE IV-19

MELTING POINT ISOTHERMS

$UO_2(NO_3)_2-HNO_3-Al(NO_3)_3-H_2O$ SYSTEMS

SOUR[redacted]W-10580

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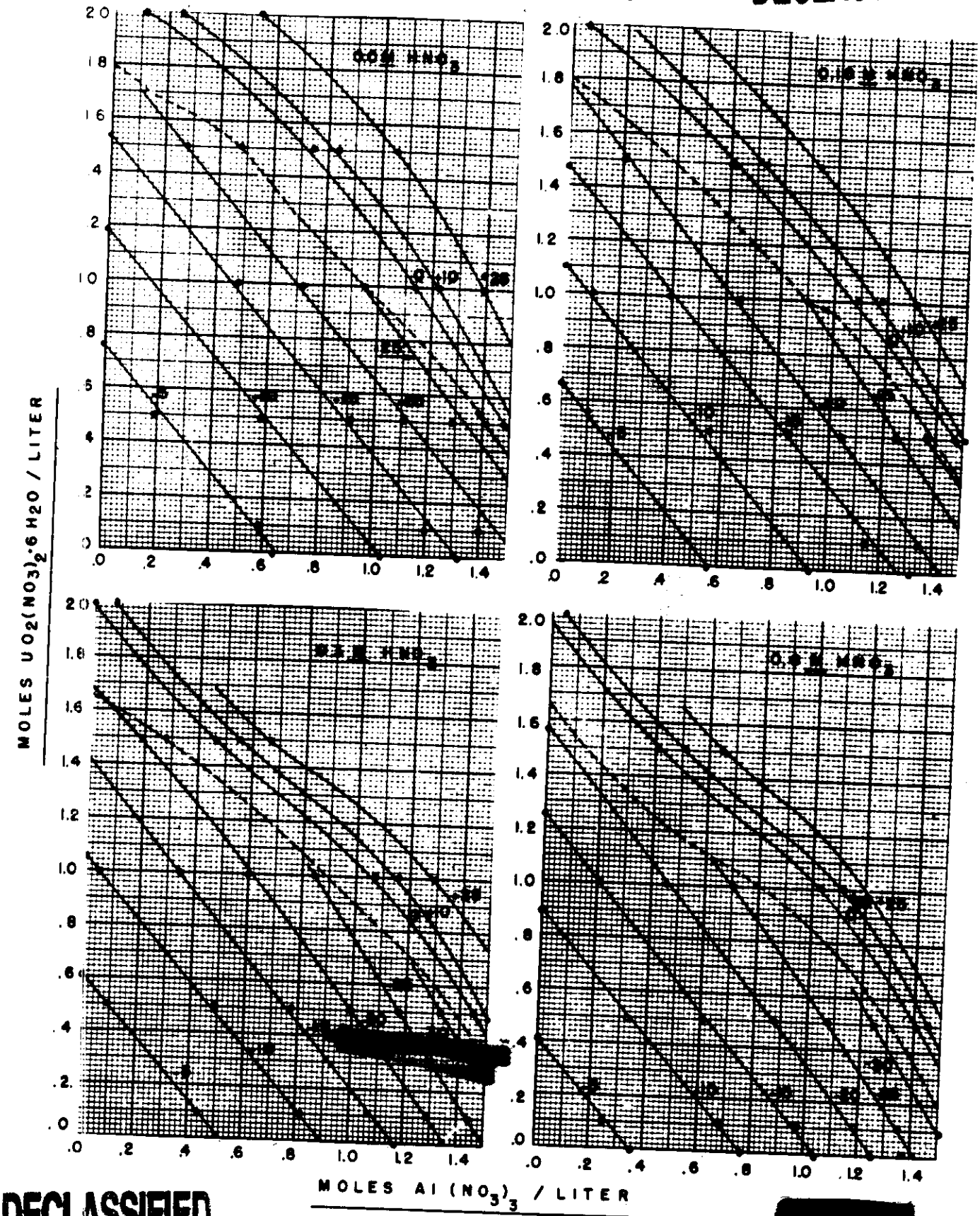

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EVAPORATION OF SIMULATED IAW(140)

ANL June,1948 (Acid) Flowsheet

Composition of Feed: 0.63 M $Al(NO_3)_3$, 0.63 M HNO_3

Cut No.	Vapor Temperature, °C.	Overhead Volume % of Charge	Overhead HNO_3, M	Residue Volume % of Charge	Residue Composition, M $Al(NO_3)_3$	Residue Composition, M HNO_3	Cumulative % of HNO_3 Vaporized
Charge	---	-----	---	100.0	0.63	0.63	0
1	99.5	0-25.0	0.01	75.0	0.84	0.83	2
2	102.8	25.0-50.0	0.04	50.0	1.26	1.23	3
3	103.3	50.0-52.6	0.08	47.4	1.33	1.29	3
4	104.0	52.6-55.0	0.11	45.0	1.40	1.35	3
5	104.5	55.0-57.5	0.15	42.5	1.48	1.42	5
6	105.0	57.5-60.0	0.20	40.0	1.57	1.50	5
7	105.6	60.0-62.5	0.27	37.5	1.68	1.58	6
8	106.7	62.5-65.3	0.39	34.7	1.81	1.68	8
9	107.8	65.3-67.5	0.56	32.5	1.94	1.75	9
10	108.9	67.5-70.0	0.76	30.0	2.10	1.84	13
11	110.5	70.0-72.5	1.12	27.5	2.29	1.90	17
12	111.6	72.5-75.0	1.61	25.0	2.52	1.93	24
13	112.9	75.0-77.7	2.40	22.3	2.82	1.88	33
14	113.9	77.7-80.1	3.28	19.9	3.16	1.70	54
15	115.0	80.1-82.5	4.28	17.5	3.60	1.33	64
16	117.9	82.5-87.4	5.74	12.6	5.00	---	---

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FIGURE IV-21

SPECIFIC HEATS OF AQUEOUS PROCESS SOLUTIONS

SOURCE OF DATA. $Al(NO_3)_3$ AND $UO_2(NO_3)_2$—CHEMICAL RESEARCH SECTION UNPUBLISHED REPORT; HNO_3—I.C.T.

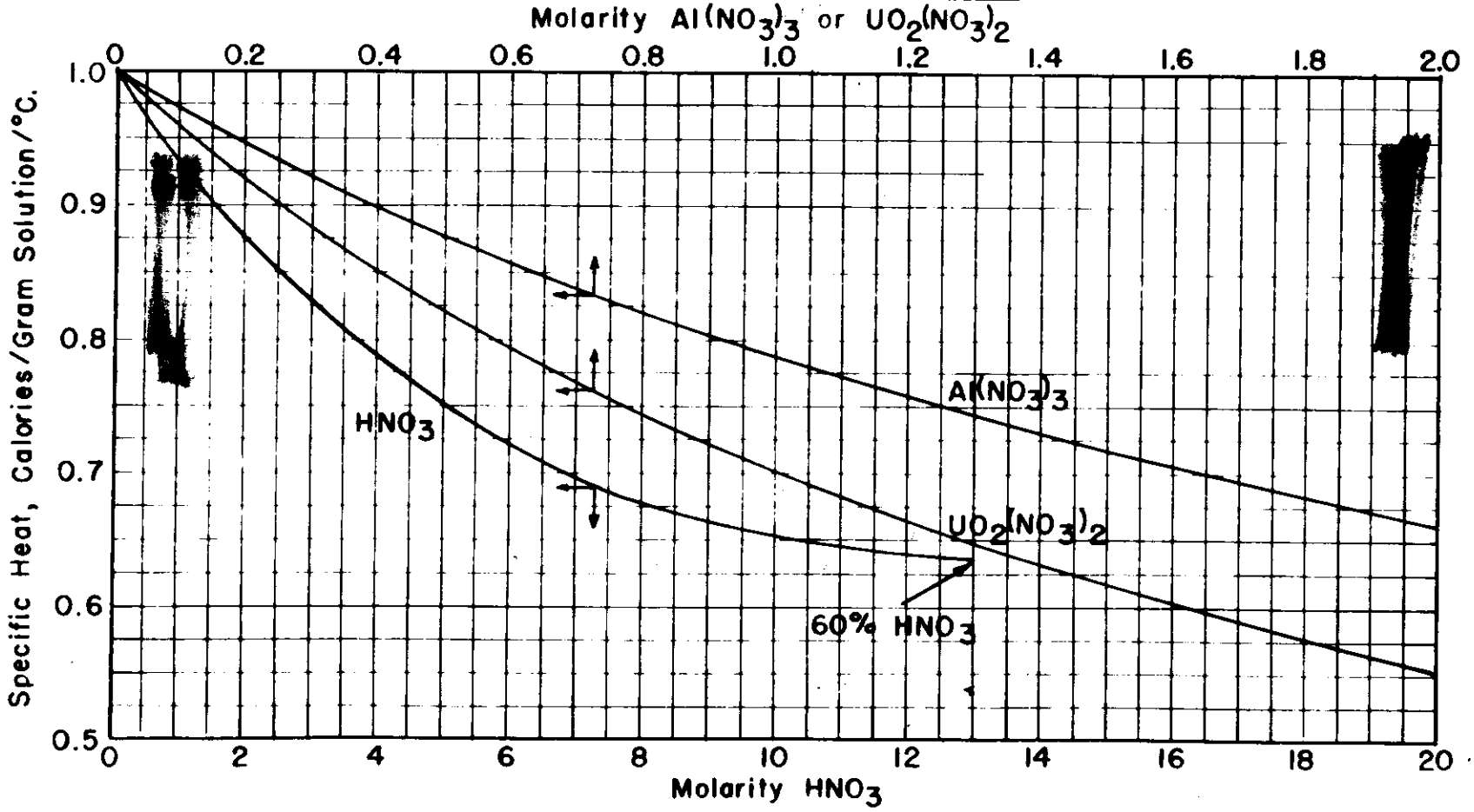

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FIGURE IV-21

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TABLE IV-22

EQUATIONS FOR THE SOLUBILITY OF HEXONE IN $UO_2(NO_3)_2$-$Al(NO_3)_3$-HNO_3-H_2O SYSTEMS (166)

Weight % Hexone = $S_0 + f_1(t)\underline{M}_{Al(NO_3)_3} + f_2(t)\underline{M}_{UO_2(NO_3)_2} + f_3(t)\underline{M}_{HNO_3}$

Temperature, °C.	S_0	$f_1(t)$	$f_2(t)$	$f_3(t)$
0	2.92	-0.992	-0.751	+0.499
10	2.38	-0.806	-0.551	+0.402
20	2.01	-0.677	-0.411	+0.332
25	1.87	-0.626	-0.356	+0.304
30	1.75	-0.586	-0.311	+0.281
40	1.60	-0.528	-0.248	+0.246
50	1.51	-0.495	-0.210	+0.222
60	1.50	-0.485	-0.195	+0.207
70	1.55	-0.495	-0.203	+0.201
80	1.66	-0.521	-0.227	+0.202
90	1.83	-0.568	-0.272	+0.210
100	2.05	-0.630	-0.333	+0.233
110	2.33	-0.713	-0.415	+0.244
120	2.67	-0.812	-0.513	+0.269
130	3.08	-0.931	-0.632	+0.302

t = °C.
$\underline{M}$ = Molarity of the species indicated by subscript position.

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FIGURE IV-23

BOILING POINTS AND FREEZING POINTS

$UO_2(NO_3)_2-H_2O$ SYSTEM

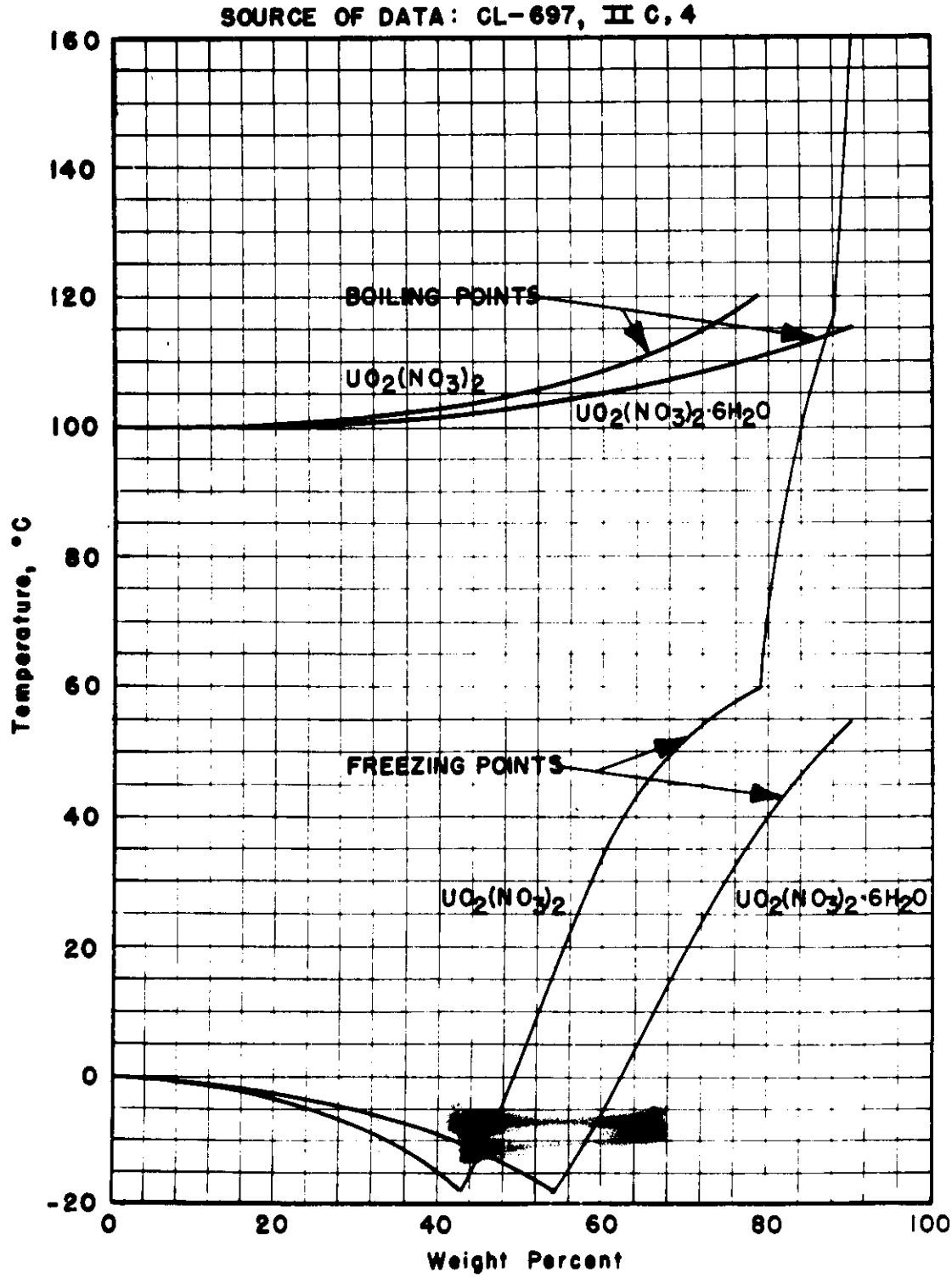

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FIGURE IV - 24

FREEZING POINTS AND SOLUBILITY

$UO_2(NO_3)_2 - HNO_3 - H_2O$ SYSTEMS

SOURCE OF DATA: HW-8309

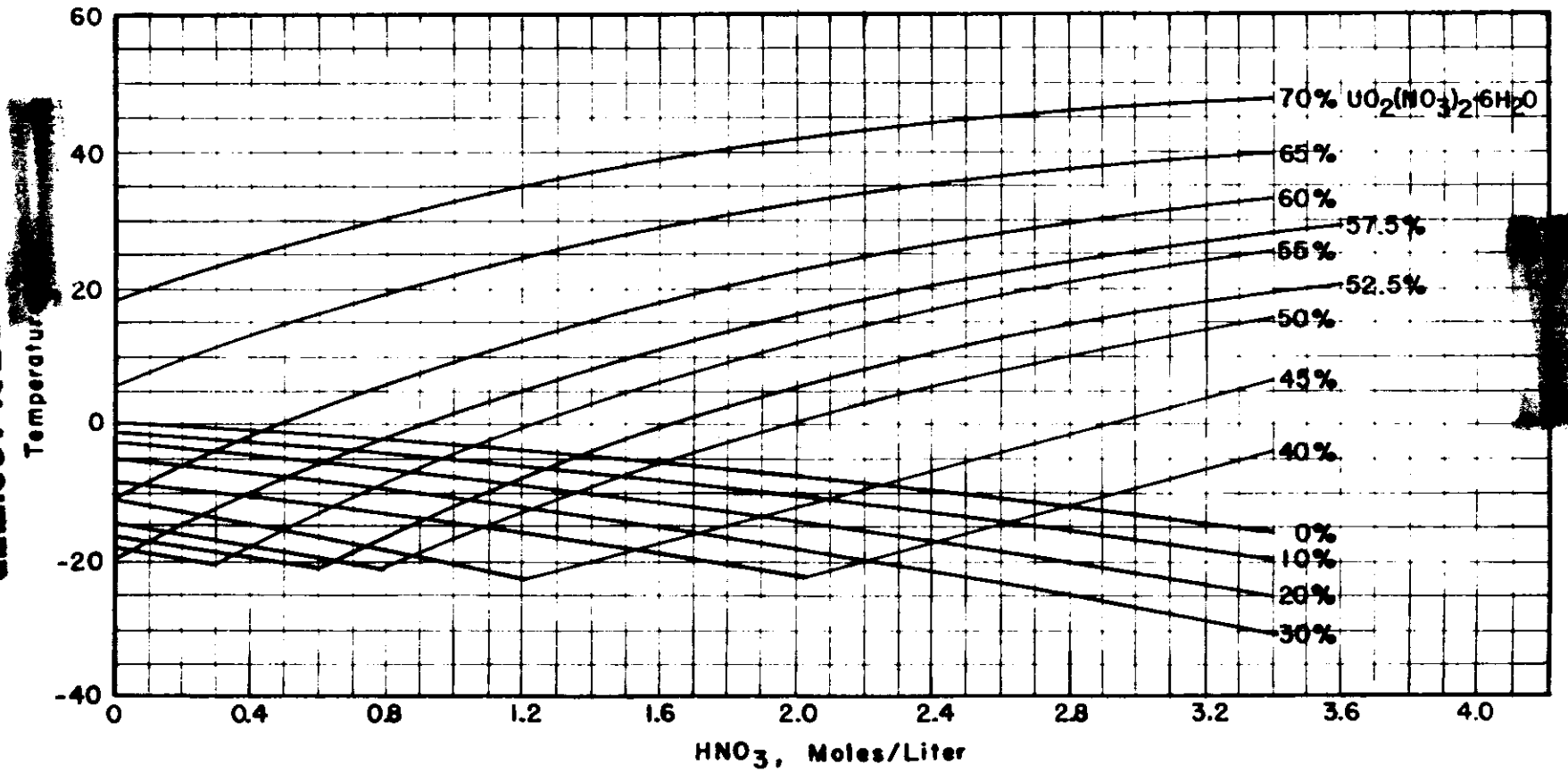

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FIGURE IV-24

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TABLE IV-25

AQUE[redacted] PROFILES

LABORATORY COUNTERCURRENT BATCH EQUILIBRATIONS

A. Redox IA Column[c]

Stage	ANL June, 1948 Flowsheet[b]	ORNL June, 1949 Flowsheet[c]	HW No. 4 Flowsheet[d]
Scrub Section			
1	1.2688	1.3036	1.2951
2	1.2785	1.3036	1.2918
3	1.2831	1.3037	1.2924
4	1.2826	1.2918	1.2924
Extraction section			
5	1.3361	1.3020	1.3191
6	1.2594	1.2432	1.2540
7	1.2202	1.2124	1.2259
8	1.1874	1.2003	1.2083
9	1.1708	1.1893	1.1974
10	1.1538	1.1802	1.1856
11	1.1471	1.1757	1.1761
12	1.1398	1.1713	1.1739
13	1.1414	1.1705	1.1726
14	1.1340	1.1665	1.1720
15	1.1375	1.1728	- - -
16	1.1357	1.1680	- - -

B. Redox IC Column[a]

Stage	ANL June, 1948 Flowsheet[e]
1	1.008
2	1.070
3	1.192
4	1.289

(a) Densities are given in g./ml. IA and IC Column entering stream compositions are given in Table IV-2 for the respective flowsheets. The complete flowsheets are presented in Chapter I.

(b) Source of data: HW-10596(150).

(c) Source of data: HW-15209(175).

(d) Source of data: HW-14984(173).

(e) Source of dat[redacted] HW-16773(188).

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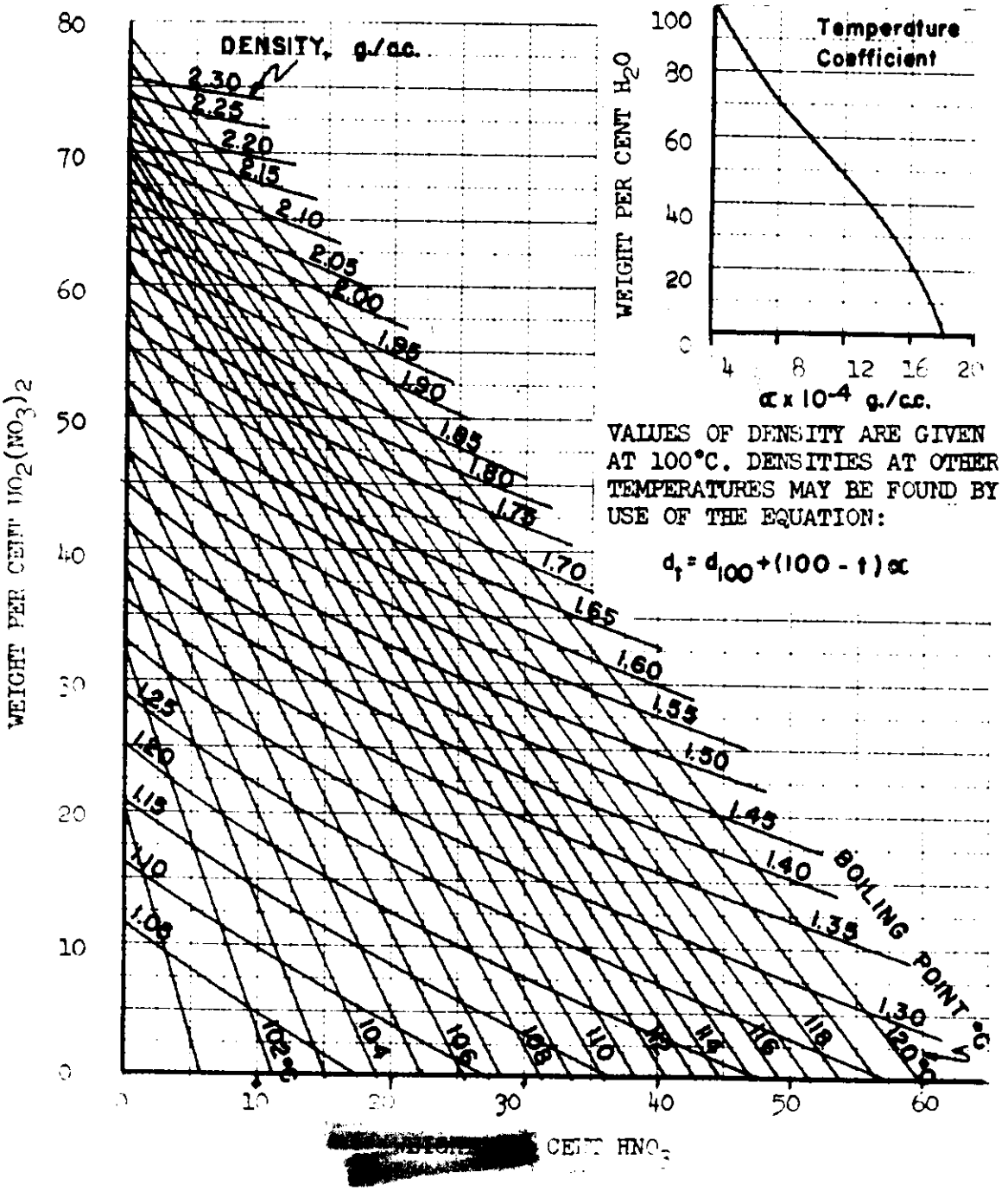
FIGURE IV-26

BOILING POINT AND DENSITY

H_2O-$UO_2(NO_3)_2$-HNO_3 SYSTEMS

(Data from CL-697 IIc, 4)



VALUES OF DENSITY ARE GIVEN AT 100°C. DENSITIES AT OTHER TEMPERATURES MAY BE FOUND BY USE OF THE EQUATION:

$$d_t = d_{100} + (100 - t)\alpha$$

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FIGURE IV-27

pH AT 25°C. OF AQUEOUS SOLUTIONS OF $UO_2(NO_3)_2$, HNO_3 ($NaOH$), AND $Al(NO_3)_3$

SOURCE OF DATA: HW-14559

$Al(NO_3)_3$ Molarity: ● 0.0M, △ 0.5M, × 0.825M, ⊡ 1.0M, ⊙ 1.3 M, ⊙ 1.5M, ◇ 2.0M. (POINTS SHOWN ARE FOR IDENTIFICATION ONLY)

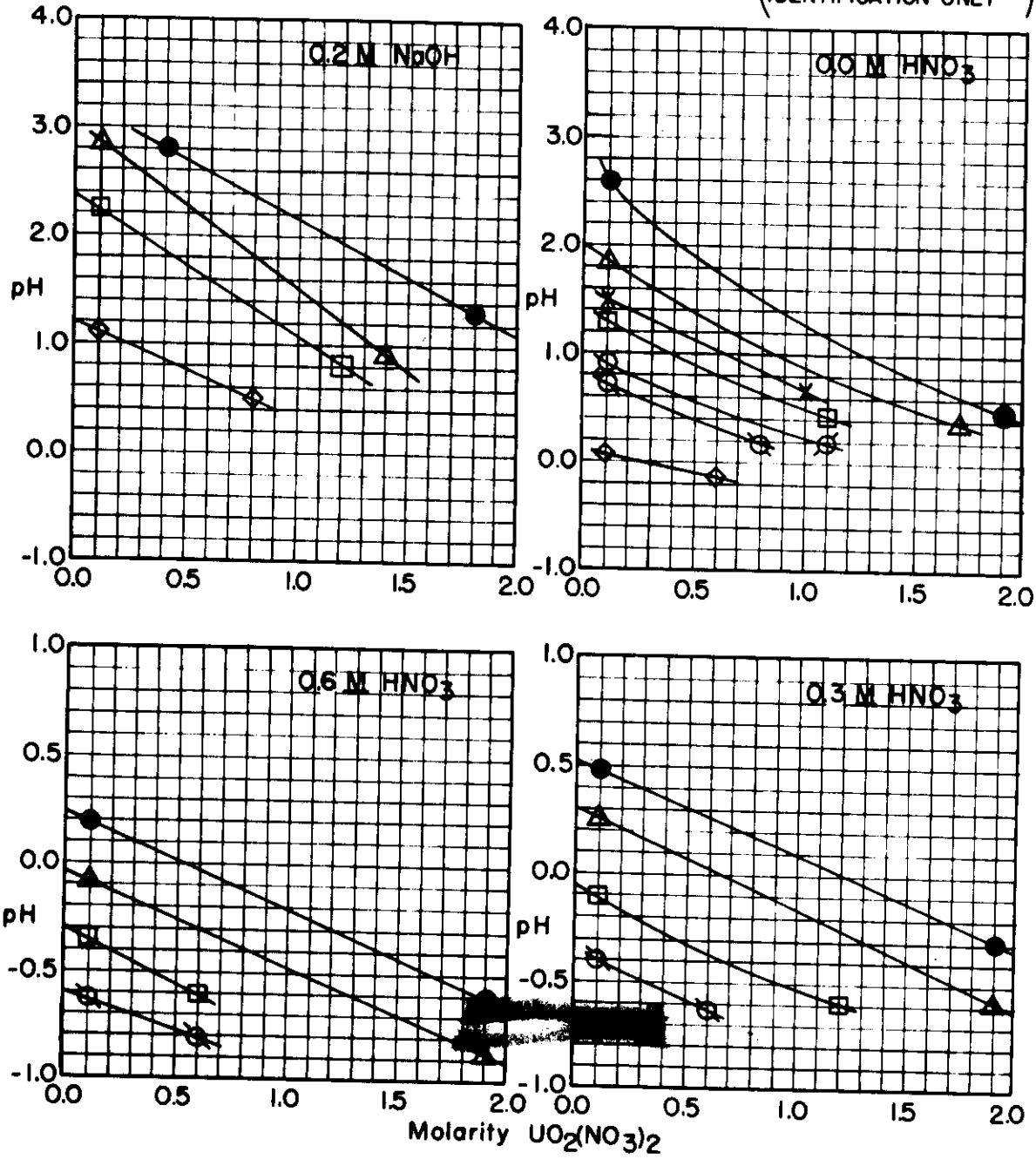

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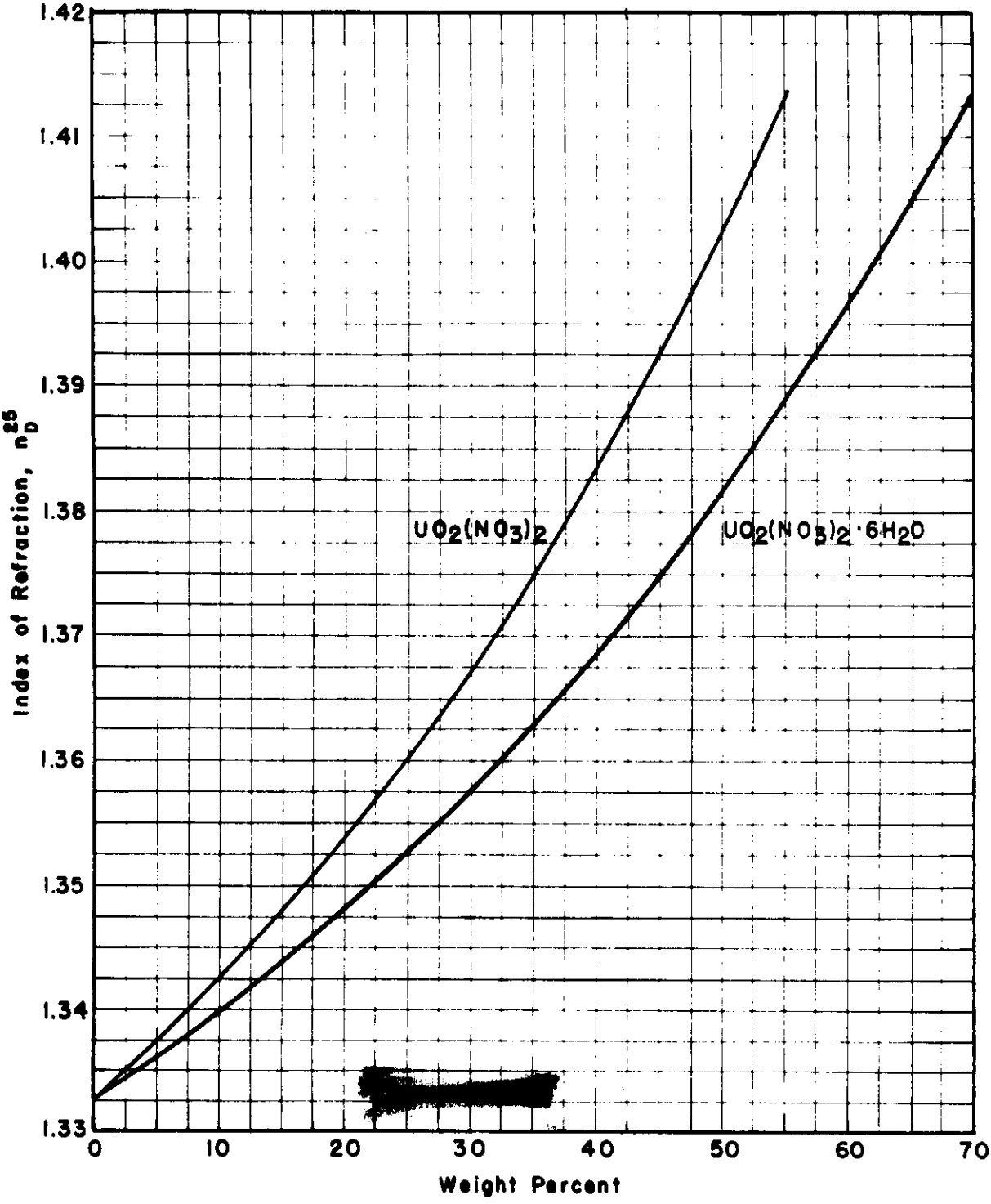
FIGURE [redacted] 28

REFRACTIVE INDICES OF $UO_2(NO_3)_2$ SOLUTIONS

SOURCE OF DATA: CL-697, II C, 4



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PHYSICAL PROPERTIES OF URANIUM NITRATE-WATER SOLUTIONS

Heat of Solution

(Project Handbook, GL-697, IIC, 4.1)

Salt	Molecular Weight	Q, Heat of Solution One Mole Salt in 220 Moles H_2O	
		Kcal/Mole	B.T.U./Lb.
$UO_2(NO_3)_2$	394.1	19	86.8
$UO_2(NO_3)_2.H_2O$	412.1	11.87	51.9
$UO_2(NO_3)_2.2H_2O$	430.1	5.05	21.1
$UO_2(NO_3)_2.3H_2O$	448.1	1.35	5.43
$UO_2(NO_3)_2.6H_2O$	502.2	-5.25	-18.8

(Heat evolved for positive Q)

Diffusion Coefficient at 20°C.

(Project Handbook, GL-697, IIC, 4.1)

Concentration, Wt.% Uranium Nitrate	Diffusion Coefficient into Water at 20°C., Sq.Cm./Day
4	0.687
9.3	0.670
17	0.661
29.8	0.664
48	0.670

For 0.4 M $UO_2(NO_3)_2$ at 18°C.:

(From I.C.T. 3. 66 (1929))

Diffusion into water: 0.58 sq.cm./day

Diffusion into 8 M HNO_3: 0.44 sq.cm./day

Partial Pressures

(Project Handbook, GL-697, IIC, 4.1)

Concentration, Wt.% $UO_2(NO_3)_2$	Partial Pressure of H_2O, Mm.Hg	
	at 25°C.	at 100°C.
12.6		746.9
18.55	23.0	[redacted]
25.7		725.1
31.7		710.7
33.1	21.8	
43.7	18.7	
55.2	17.2	

Freezing Point Lowering

(Project Handbook, GL-697, IIC, 4.1)

$UO_2(NO_3)_2$ Concentration	Freezing Point Lowering	
	°C.	°C./Mole
0.5 Molar	2.967	5.93
[redacted]	1.339	5.36
[redacted]	0.646	5.17
0.0625	0.329	5.26
0.03125	0.168	5.37

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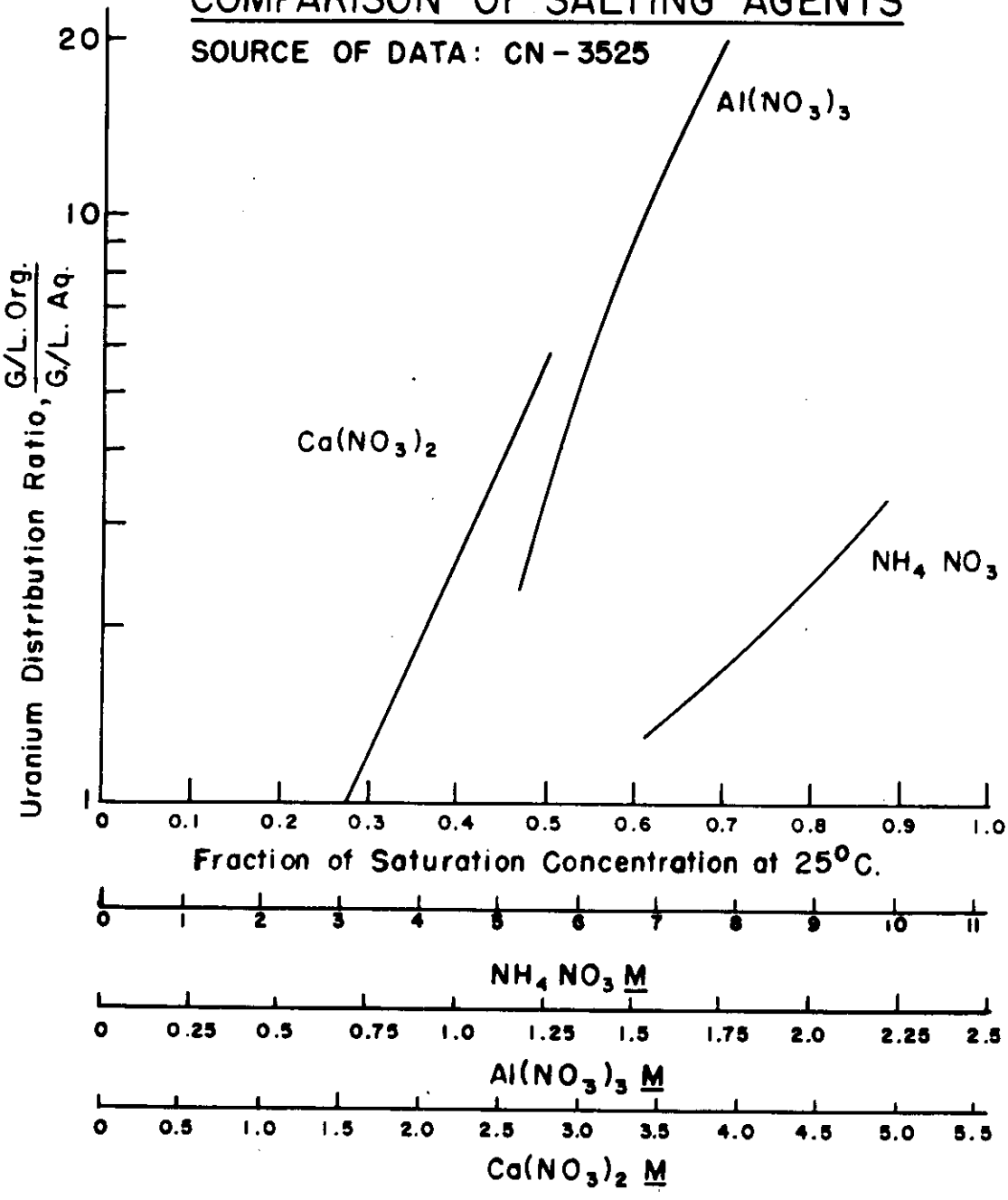
URANIUM DISTRIBUTION
COMPARISON OF SALTING AGENTS



Aqueous phase 0.61 M $UO_2(NO_3)_2$.

Equal volume extraction at 28°C.

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FIGURE IV-31

URANIUM NITRATE DISTRIBUTION

HEXONE-WATER-$UO_2(NO_3)_2$-$Al(NO_3)_3$-HNO_3 SYSTEM

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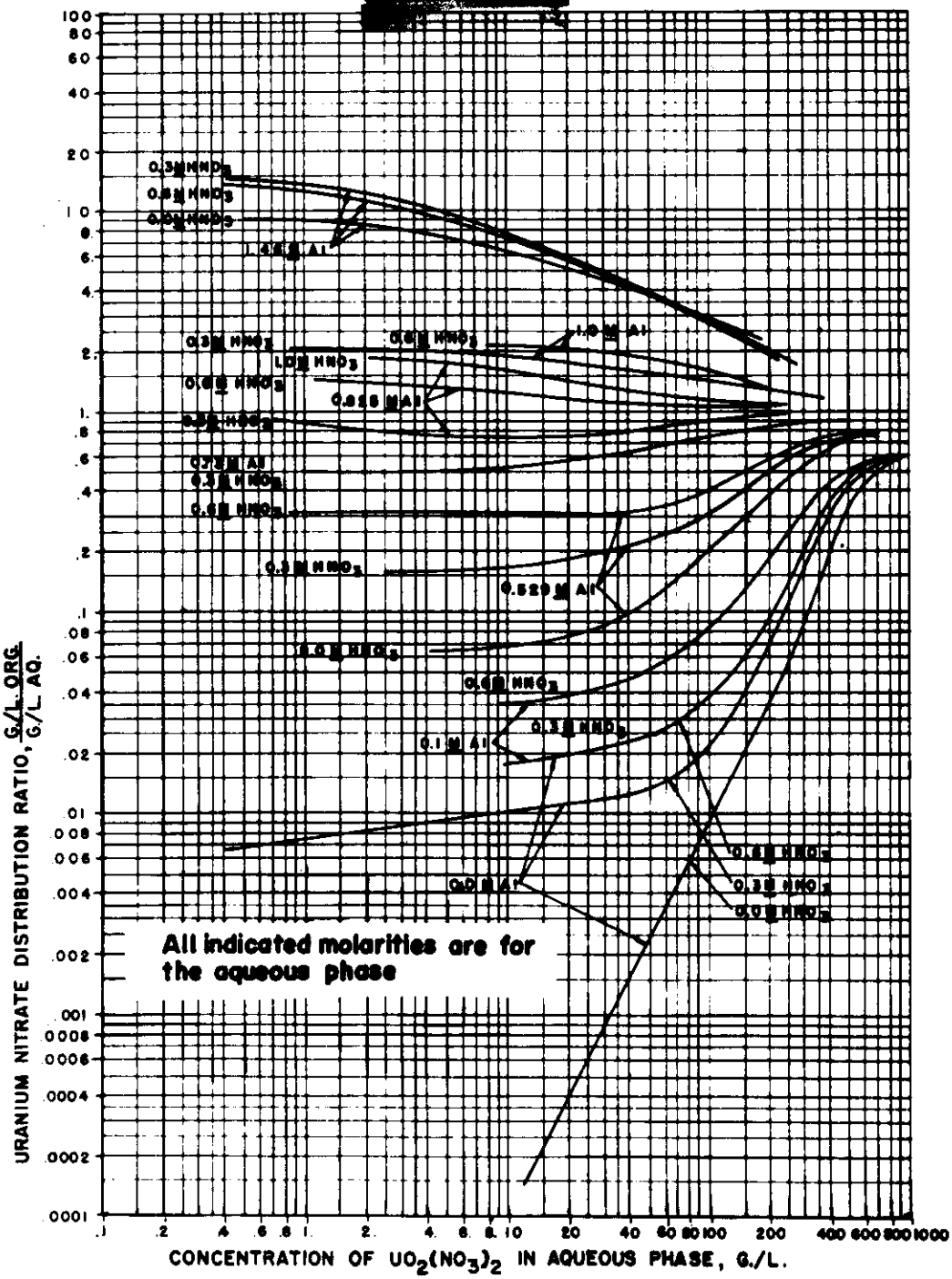

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TABLE IV-32

URANIUM AND PLUTONIUM DISTRIBUTION RATIO — ACID-DEFICIENT SYSTEM(162)

HEXONE-$UO_2(NO_3)_2$-$Al(NO_3)_3$-$Na_2Cr_2O_7$ SYSTEM

Aqueous Phase Composition, M					Distribution Ratio, G./L. Org. / G./L. Aq.	
$UO_2(NO_3)_2$	HNO_3	$Al(NO_3)_3$	NO_3^-	pH	E_a^o, Pu(VI)(a)	E_a^o, U(VI)(b)
[redacted].0	-0.197	0.5	1.50	3.15	0.045	--
.0023	-0.20	0.5	1.51	3.15	0.021	0.136
.024	-0.18	0.5	1.55	2.98	0.026	0.016
.097	-0.195	0.5	1.69	2.82	0.040	0.034
.95	-0.22	0.5	3.4	1.65	0.040	0.57
[redacted]0	-0.17	1.0	3.00	2.47	1.11	--
0.0025	-0.18	1.0	3.005	2.47	0.37	0.37
0.025	-0.17	1.0	3.05	2.26	0.28	0.36
0.1	-0.14	1.0	3.20	2.30	0.36	0.52
0.98	-0.18	1.0	4.96	1.14	0.89	1.08
0.0	-0.20	2.0	6.00	1.20	38.8	--
0.00046	-0.16	2.0	6.00	1.15	18.2	33.4
0.00476	-0.19	2.0	6.01	1.12	11.7	20.7
0.037	-0.17	2.0	6.08	1.09	7.78	15.6
0.47	-0.27	2.0	6.94	0.92	2.16	2.90
0.2	-0.20(c)	1.0	3.2	2.2	0.38	0.60
1.1	-0.20(c)	1.0	5.0	1.1	0.79	1.09

(a) Pu(VI) distribution determined in the presence of 0.05 M $Na_2Cr_2O_7$.

(b) U(VI) distribution determined in the absence of $Na_2Cr_2O_7$ and Pu.

(c) Solutions made 0.20 M acid deficient by the addition of UO_3 instead of NaOH.

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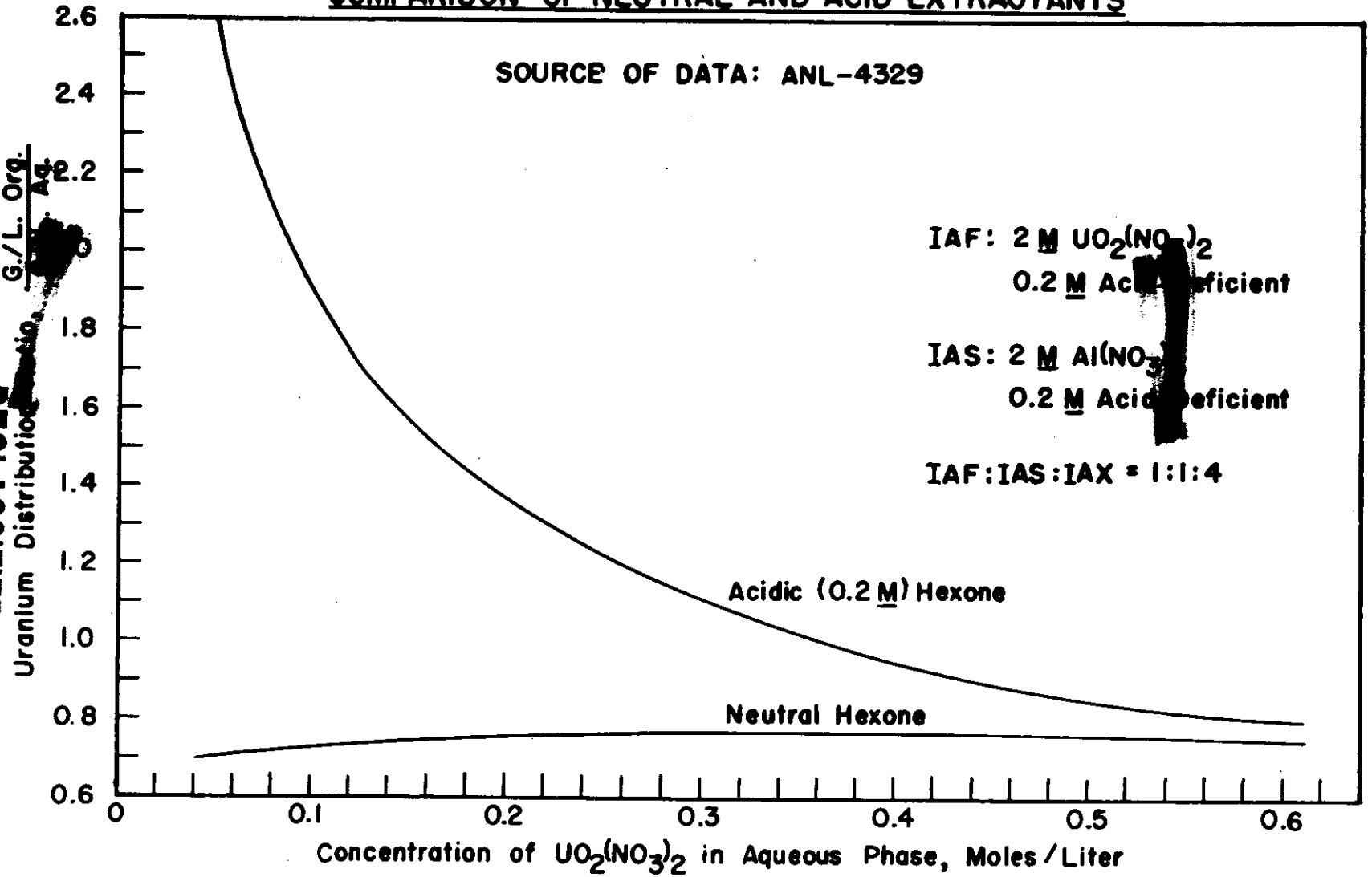
FIGURE IV-33
URANIUM DISTRIBUTION
IA COLUMN SYSTEM
COMPARISON OF NEUTRAL AND ACID EXTRACTANTS



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URANIUM DISTRIBUTION
EFFECT OF TEMPERATURE

Curve	Source	Concentration M./L. (Aqueous Phase)				
		UNH	HNO_3	$Al(NO_3)_3$	$NaNO_3$	$Na_2Cr_2O_7$
1	A-2329	0.2	0.0	1.5	0.0	0.0
2	MonN-319	0.02	0.45	1.25	0.0	0.1
3	HW-14448	1.5	0.0	0.0	2.0	0.0
4	HW-11417	1.4	0.4	0.0	0.0	0.0
5	HW-11417	1.5	0.0	0.0	0.0	0.0
6	HW-14448	0.5	0.0	0.0	2.0	0.0

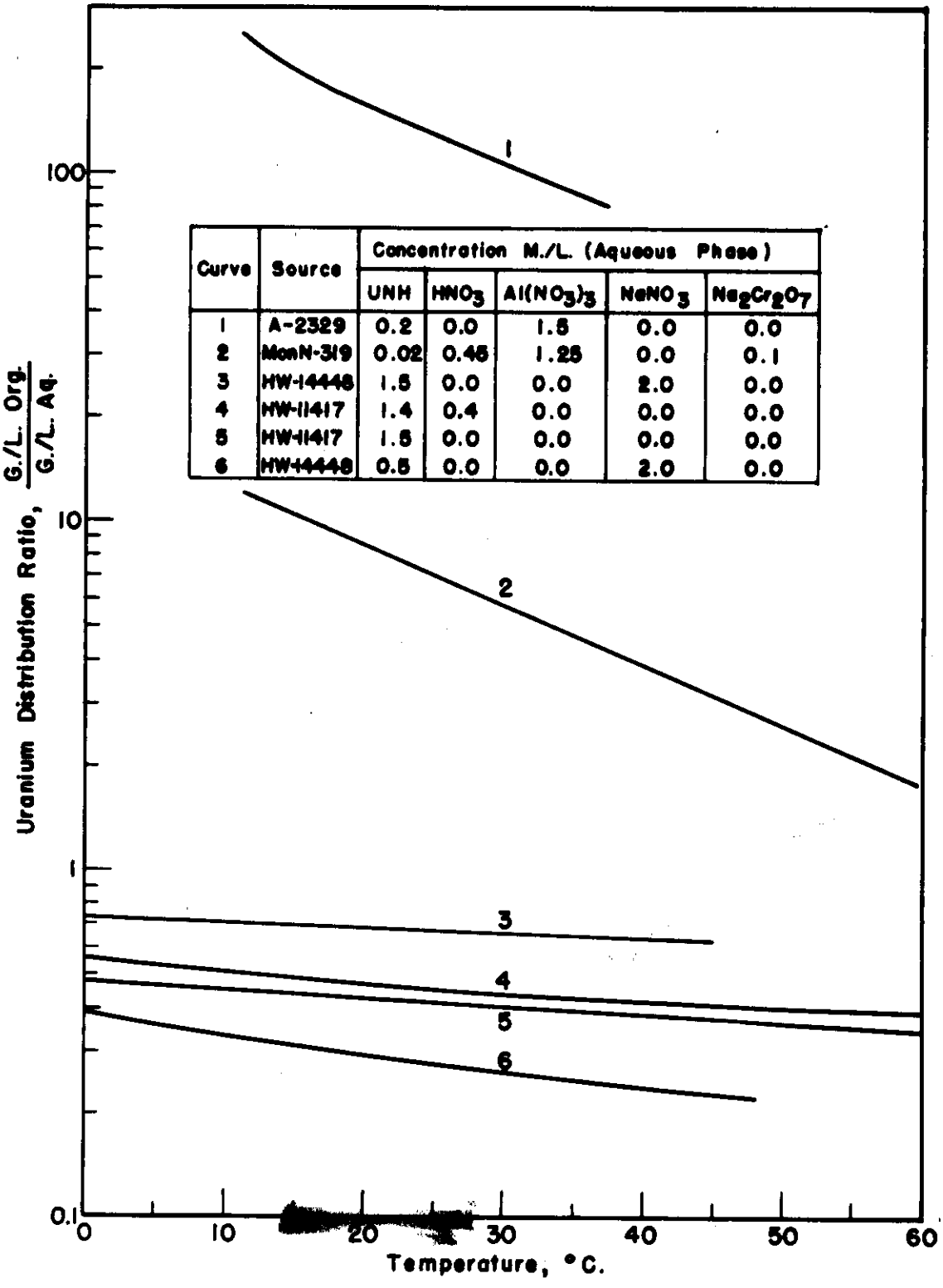

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TABLE IV-35

URANIUM AND PLUTONIUM DISTRIBUTION

EFFECT [redacted] RITIES (174)

Aqueous Phase: 1.0 M $Al(NO_3)_2$, 0.0 M HNO_3 and $UO_2(NO_3)_2$ as listed. The initial aqueous solution contained 5 to 20 mg. Pu/liter with 0.05 M $Na_2Cr_2O_7$ used as the holding oxidant for Pu(VI).

Parenthetical values are distribution ratios in corresponding solutions in absence of impurity.

Impurity in Hexone	$UO_2(NO_3)_2$ in Equilibrated Aqueous Phase, M	Distribution Ratio, G./L. Org. / G./L. Aq. $UO_2(NO_3)_2$	Pu(VI)	Pu(IV)
0.60 M acetic acid[a]	0.933	1.225 (1.20)	1.066 (0.89)	---
0.60 M acetic acid[a]	0.096	1.147 (1.15)	1.13 (0.59)	---
0.60 M acetic acid[a]	0.003	1.013 (0.96)	1.476 (0.62)	---
37 g./l dinitroisobutane + 28 g./l. diketone[b]	0.482	1.059 (1.18)	0.679 (0.82)	0.257 (0.243)
37 g./l. dinitroisobutane + 28 g./l. diketone[b]	0.022	0.75 (0.65)	0.544 (0.47)	0.514 (0.161)
5 g./l. ethyl nitrolic acid	0.445	1.28 (1.18)	---	0.427 (0.243)
5 g./l. ethyl nitrolic acid	0.003	0.589 (0.96)	0.966 (0.62)	0.160 (0.247)
10 g./l. oxime[c]	0.448	1.19 (1.18)	---	0.294 (0.243)
10 g./l. oxime[c]	0.002	0.996 (0.961)	0.637 (0.62)	0.226 (0.247)

(a) Aqueous phase equilibrated with respect to acetic acid.
(b) Methyl isopropyl [redacted] ketone.
(c) Alpha isonitroso [redacted] ketone.

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FIGURE IV-36

UR[redacted]IBRIUM

[redacted]YSTEM

COMPARISON OF FLOWSHEETS

SOURCE OF DATA: HW-14984, 15209, AND 10596

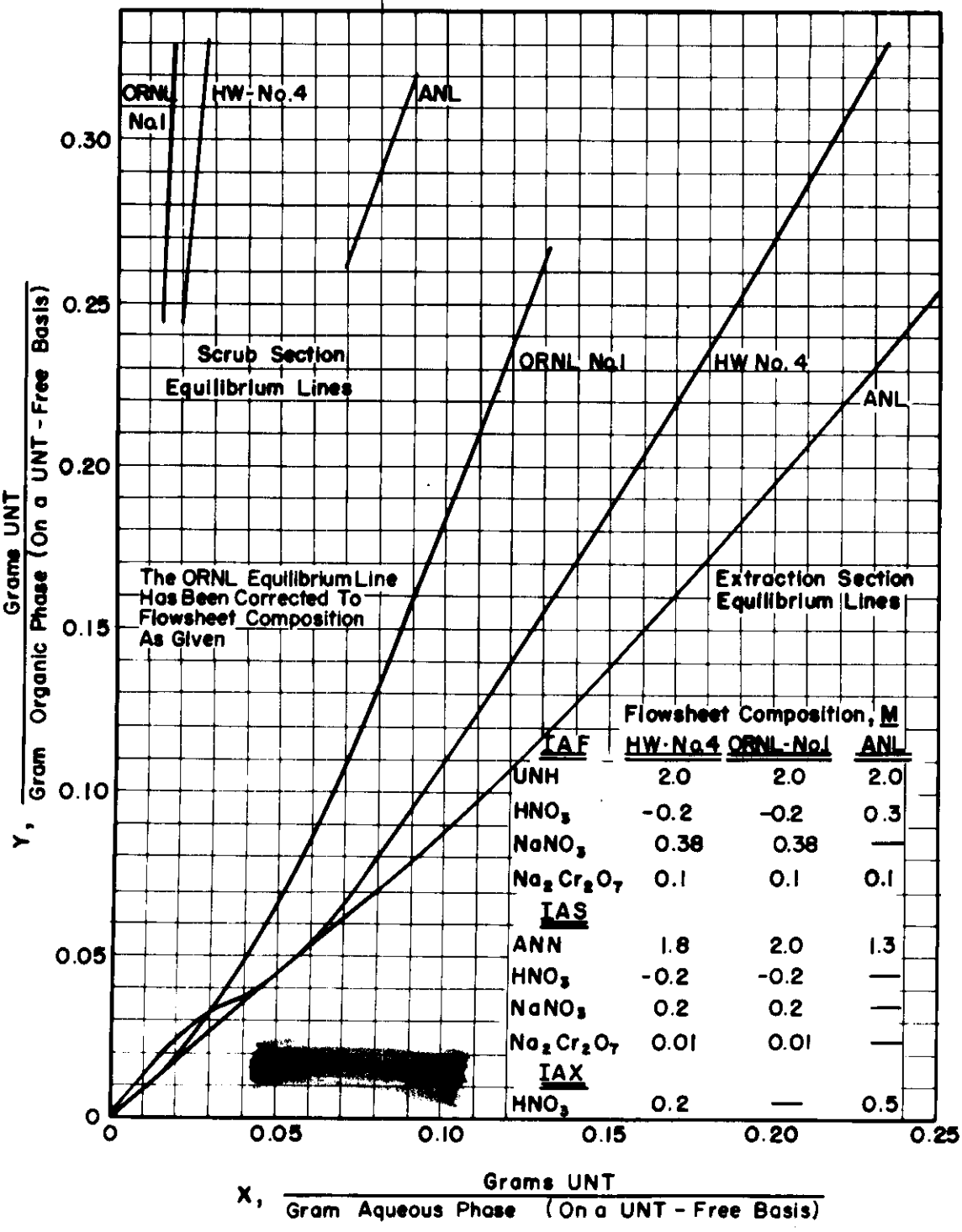

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FIGURE IV-37

URANIUM EQUILIBRIUM

IA COLUMN SYSTEM

HW-NO. 4 FLOWSHEET

SOURCE OF DATA: UNPUBLISHED DATA OF HANFORD WORKS CHEMICAL DEVELOPMENT AND CHEMICAL RESEARCH SECTIONS

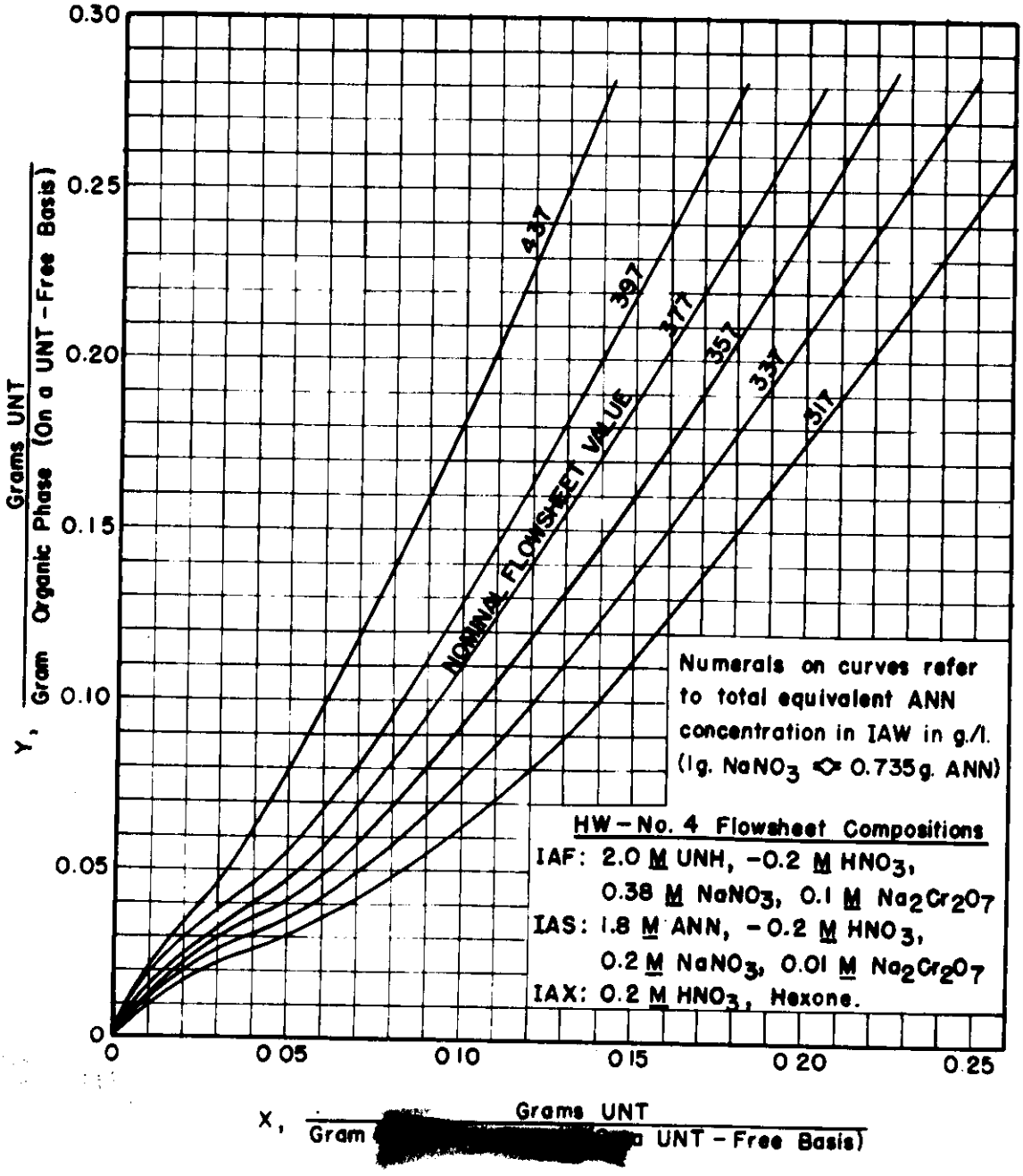

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FIGURE IV-38

URANIUM EQUILIBRIUM
IA COLUMN SYSTEM
ORNL-NO.1 FLOWSHEET

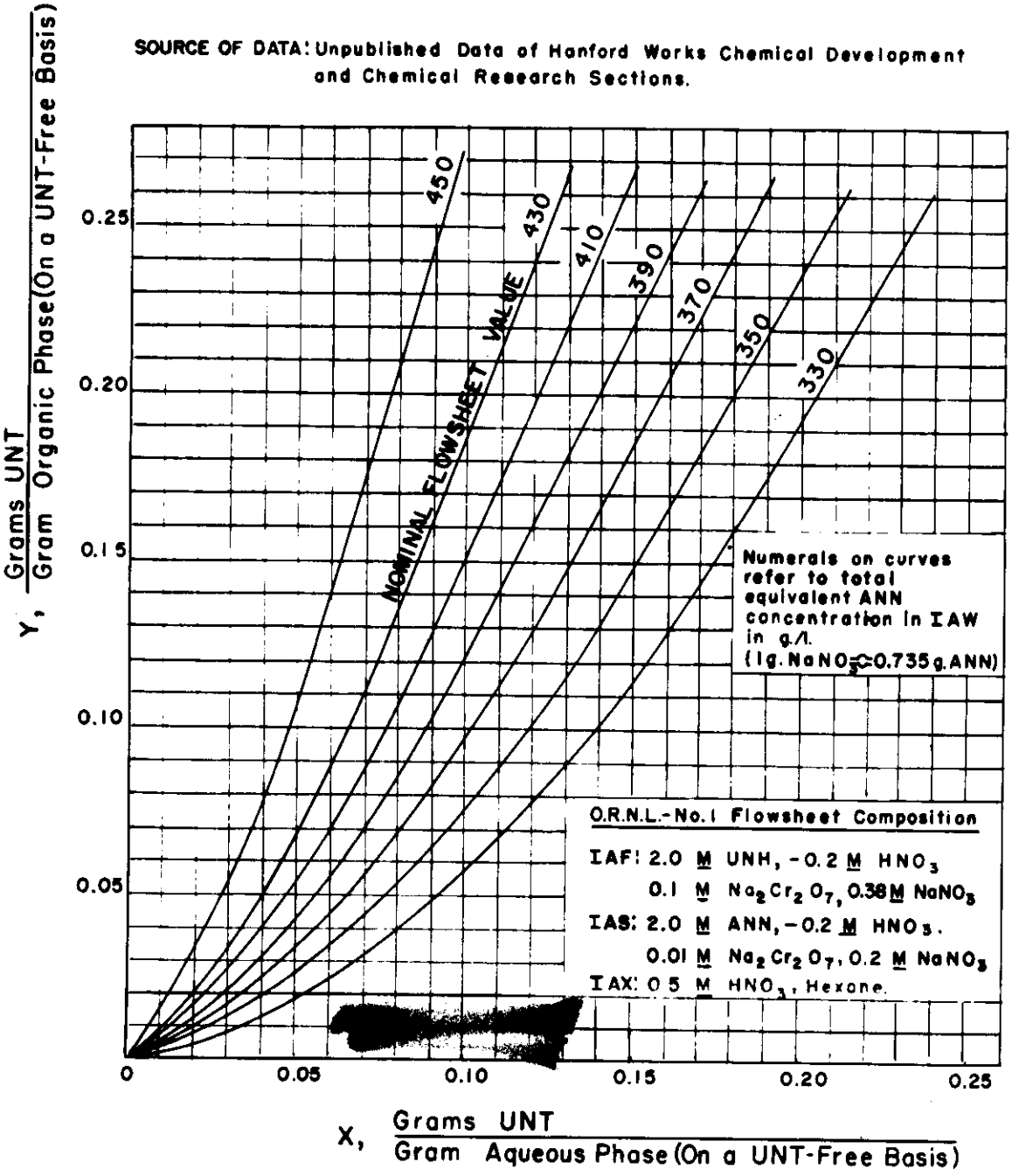

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FIGURE IV-39

URA[redacted] EQUILIBRIUM

IA COLUMN SYSTEM

ANL JUNE 1, 1948 FLOWSHEET

SOURCE OF DATA: HW-10596

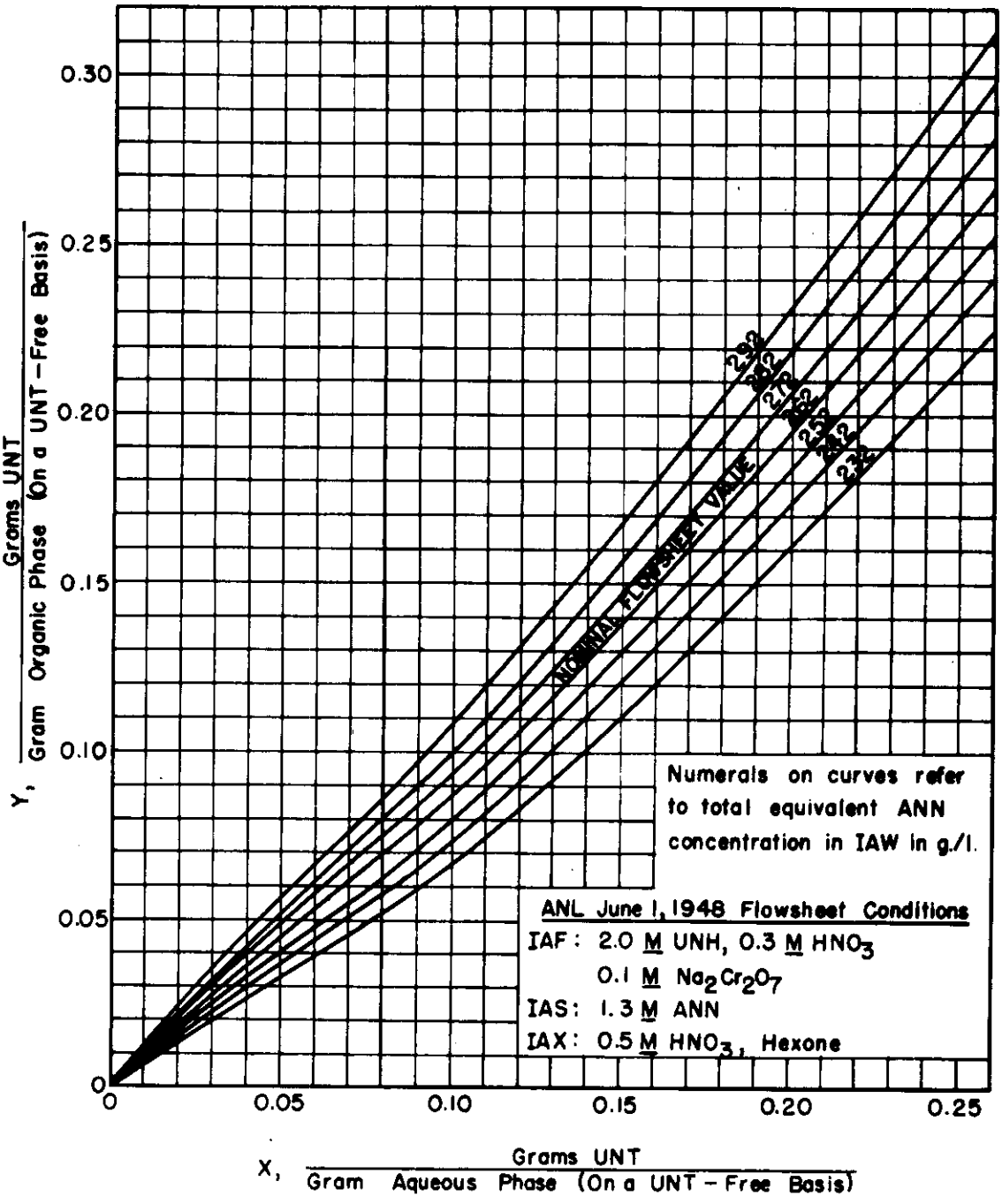

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FIGURE [redacted]

URANIUM DISTRIBUTION
IC COLUMN SYSTEM
EFFECT OF HNO_3 CONCENTRATION

SOURCE OF DATA: HW-18773

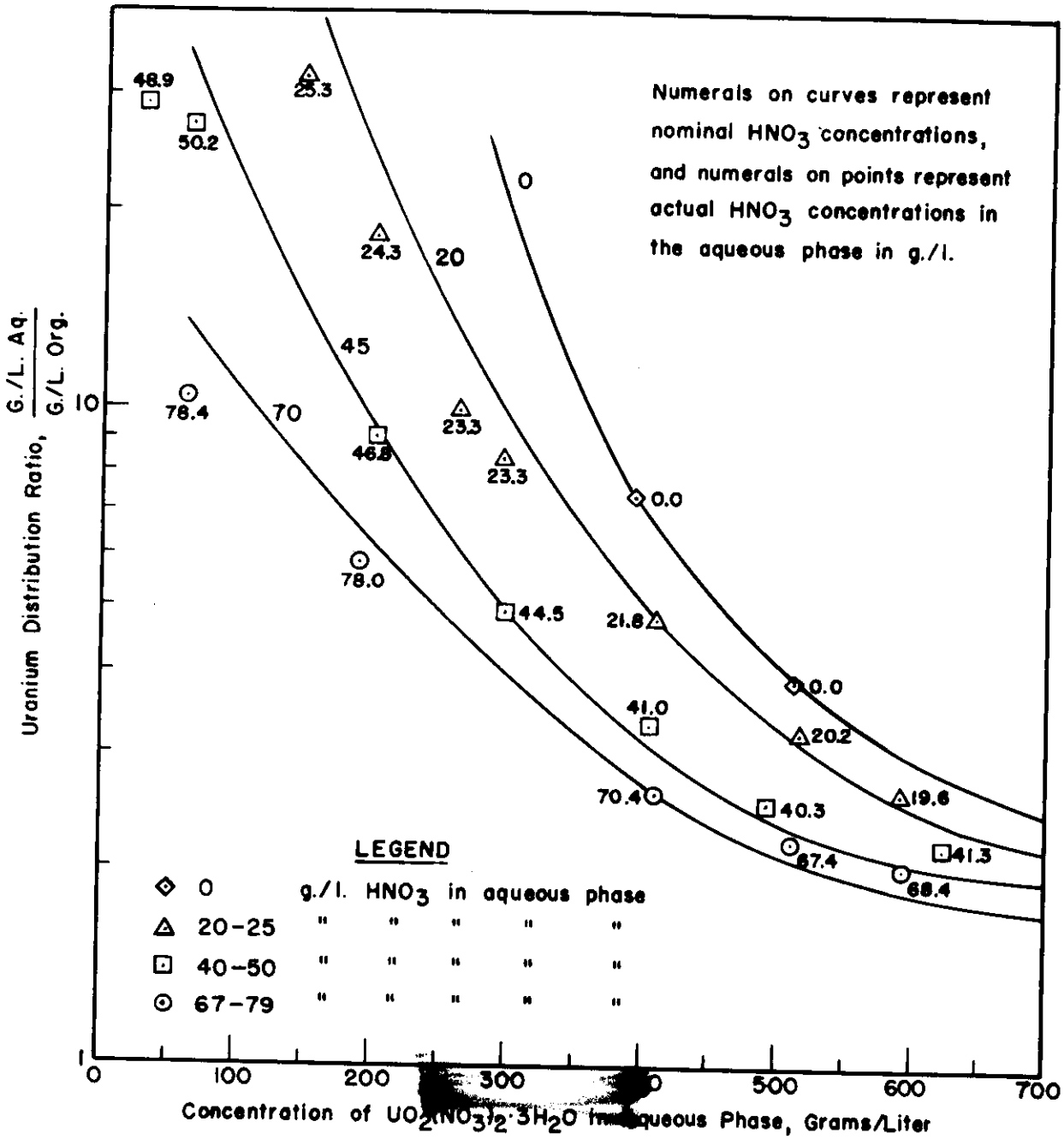

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FIGURE IV-41
URANIUM EQUILIBRIUM
IC COLUMN SYSTEM
EFFECT OF HNO_3 CONCENTRATION

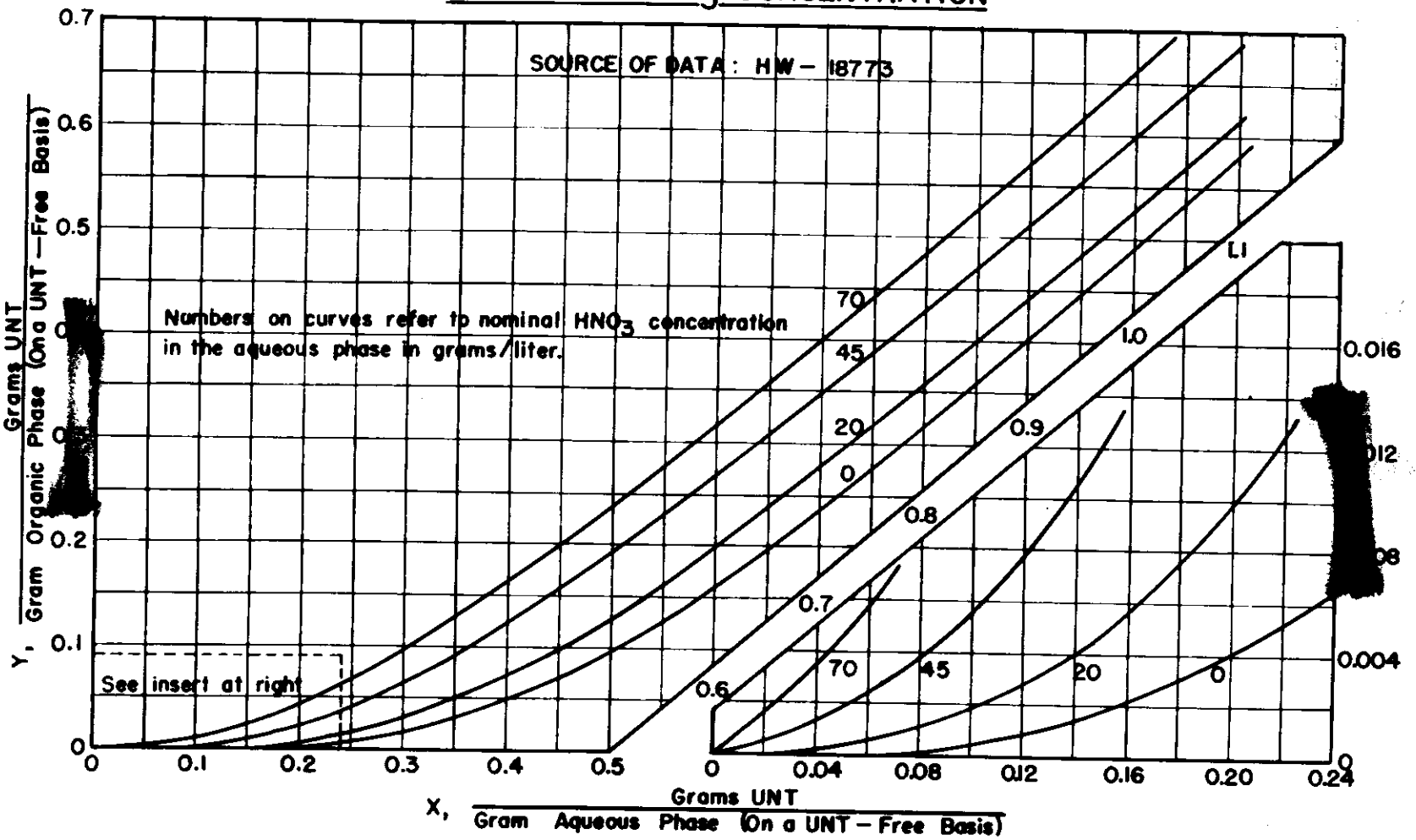

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FIGURE IV-41

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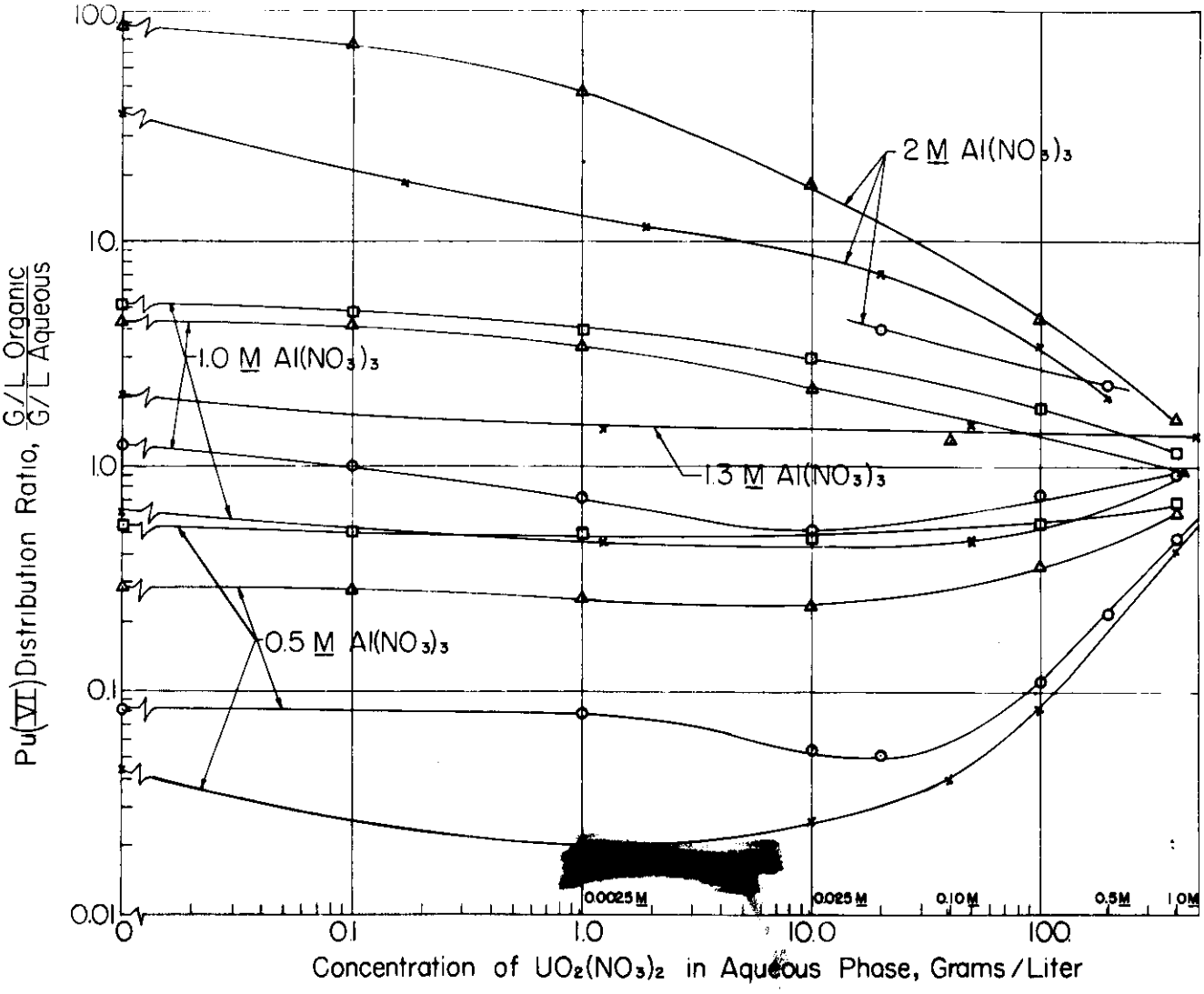
FIGURE IV-42

PLUTONIUM (VI) DISTRIBUTION
EFFECT OF $UO_2(NO_3)_2$, HNO_3, AND $Al(NO_3)_3$ CONCENTRATION

SOURCE OF DATA: HW-13760

X = - 0.2 M HNO_3
○ = 0.0 M HNO_3
△ = 0.3 M HNO_3
□ = 0.6 M HNO_3



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